

Review of past and on-going work on urban air quality in India

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**For more information about this report, please contact
Centre for Environmental Studies**

T E R I

Darbari Seth Block

Habitat Place, Lodhi Road

New Delhi – 110 003 / India

Telephone +91 11 468 2100 or 468 2111

E-mail mailbox@teri.res.in

Fax +91 11 468 2144 or 468 2145

Web site www.teriin.org

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Executive summary

This report has reviewed past (since 1990) and on-going work in India that can be used to assess the contributions of different sources to urban air pollution (with a special focus on small particulate matter), and to pull together the existing knowledge to see what we can say with a reasonable degree of certainty, and what we do not yet know. We summarise our findings below.

Regular monitoring programmes

- The air quality monitoring network is fairly extensive. While its performance has gradually improved over the years, important gaps remain:
 - Many stations are not operational.
 - The target number of sampling days required—104 days a year—is rarely met even at operational stations.
 - The data are not comprehensively and statistically analysed for temporal and spatial trends.
 - Many stations no longer represent the type of site (such as urban “hot-spots”; areas affected by vehicle and industrial emissions; city centre pedestrian precincts and residential areas representative of population exposure; parks and suburban areas) they were originally selected for because of the changes in land use pattern, habitation and commercial activities. There is a need to relocate some stations.
 - There are significant delays in reporting the data (typically one to two years).
- Based on the data collected to date, the pollutant of concern in cities in India is particulate matter. Its concentrations have been shown to far exceed the national ambient air quality standards in city after city.
- The pollutants being monitored should be reconsidered. In particular, instead of monitoring total suspended particles (TSP) which are now widely acknowledged not to be important from the point of view of public health impact, smaller particles such as PM₁₀ (particles smaller than 10 microns) or even PM_{2.5} (particles smaller than 2.5 microns) should be monitored regularly.
- Given limited financial resources, rather than expand the monitoring programme by establishing new stations, the National Ambient Air Quality Monitoring

Programme (NAMP) should focus on improving data collection and analysis at the existing stations (specially focusing on training, ensuring that sampling frequency be met, ensuring regular calibration of flow rates and, in the case of gaseous pollutants, strictly adhering to prescribed operating procedures).

- In addition to the regular monitoring, data collection for special studies (such as source apportionment) and surveys could be carried out by the Central Pollution Control Board (CPCB) and National Environmental Engineering Research Institute (NEERI)—two organisations involved in regular air quality monitoring in India—in collaboration with other research organisations.

Studies by research organisations

- It is difficult to state whether any city has been adequately studied. In comparative terms, Agra, Calcutta, Delhi and Mumbai have been better studied among the Indian cities and towns.
- There is a tendency among government agencies and other research organisations to study only ‘hot spots’ and industrial locations (such as the ITO crossing in Delhi and Chembur in Mumbai) within the cities. There is also a tendency to sample mainly at locations close to the organisation, probably owing to resource constraints and logistical difficulties (specially true in the case of studies undertaken for thesis purposes). Consequently, we believe that an understanding of the prevailing situation in ‘typical’ residential areas—where most of the population resides for most of the time—in cities is very weak, and of background concentrations of air pollutants non-existent.

Gaseous pollutants

- Only a limited amount of data is available for ambient concentrations of ozone in India. Measured ozone concentrations have generally been found to be low in Indian cities to date.
- Many studies measuring ozone concentrations have tended to focus on traffic intersections, such as the ITO junction in Delhi. Since ozone precursors and ozone travel large distances, it is important to measure ozone away from traffic corridors. Ozone concentrations may very well be much higher in non-traffic areas.
- Of all the pollutants measured, ozone shows the most distinct temporal (including diurnal) variations that can be clearly associated with vehicular activity.
- In urban areas, automobile exhaust is cited as the primary source of volatile organic compounds (including polyaromatic hydrocarbons) together with the combustion of fossil fuels and wood.

- Levels of benzene measured have been found to be high by international standards. Because of wide variation in concentrations measured, as well as exceptionally high concentrations reported in some studies, the results obtained need to be checked and confirmed. Benzene sources have been attributed to kerosene and coal burning, and automobile exhaust.

Characterisation of particulate matter

- Most of the published work has concentrated on heavy metals, particularly lead.
- The levels of elements have been found to be correlated with the characteristics of the site and anthropogenic activities taking place in its vicinity. Soil has been cited as a significant contributor in several studies.
- Incineration has been cited as an important source of lead in addition to vehicular sources. Lead levels have been observed to decrease only along dense traffic corridors and not necessarily in other parts of urban areas. Re-suspension of dust is also an important source of airborne lead.
- Very few studies have examined the size distribution of particles. These studies have been mostly of short duration, small sample size, and have not adequately documented seasonal variation.
- There are indications from the NAMP data that PM_{10} make up one-third to two-thirds of TSP.
- $PM_{2.5}$ has been found to constitute about one-half of PM_{10} .
- One recent study which analysed for total and black carbon in PM_{10} found that total carbon accounted for about one-third of PM_{10} , which is similar to the results reported in other countries. The ratio of black carbon to total carbon was comparable to those found in the Indian Ocean Experiment (INDOEX) in February and March of 1999 at altitudes ranging from 0 to 6.5 kilometres over the Indian Ocean region. These results suggest significant contributions from the combustion of fossil fuels rather than biomass (such as wood and leaf burning).
- There is essentially no information on background particulate concentrations or the characteristics of particulate matter in background areas. The definition of “background area” relevant to Indian cities is itself lacking.

Source apportionment of particulate matter

- There are very few source apportionment studies in India and most of them are more than ten years old.
- All studies but two to date have looked at TSP. Only one study has examined PM_{10} , and another size-fractionated particles. Only one study, on TSP, has explicitly quantified source contributions.

- None of the studies have analysed particles for carbon, seriously limiting the ability to examine combustion of fossil fuels and biomass in detail.
- Most studies have confirmed that natural dust is the predominant source of TSP.
- The one study examining PM₁₀ found natural dust to be the predominant source.
- Vehicular sources have typically been lumped together with all other fossil fuel combustion sources.
- Wood and refuse burning is also identified as important sources.
- Most studies have chosen industrial locations. Typical downtown or residential areas have so far not been examined.
- Seasonal variations in source contributions have not yet been studied.
- A couple of studies have identified small stationary sources of combustion as being important.
- Agricultural sources have not been considered in any study.

Emissions inventories

- Emission factors representing typical sources in India are not available for the most part. The emission factors used contain large uncertainties.
- The data needed for computing total emissions using emission factors—such as the total number of vehicles operating on the road by vehicle type and age, annual distance travelled and fuel economy; amount of leaf and garbage burned; the number of cottage industries, their processes and fuels consumed; and the efficiency of exhaust treatment devices—are also scarce.
- There are no reliable emission inventories for PM₁₀. Where PM₁₀ emission inventories have been compiled for the same city, the results have differed considerably from study to study.

Applicable lessons from studies in other countries

- Even in the United States and elsewhere where a considerable amount of resources have been spent developing emission factors and emissions inventories, gross polluters have been found to be seriously under-estimated, and some particulate emissions, such as re-suspended road dust, cannot be reliably quantified even today.
- When extensive data collection and the chemical mass balance method have been employed to quantify small particulate source contributions, the results at times have confounded the conventional wisdom. For example, the most intensive comparison of bottom-up and top-down investigations to date, the recently completed study in Colorado, found that while the particulate emissions inventory pointed to the importance of diesel vehicle exhaust in the transport

sector, actual measurements pointed to the much greater importance of smoking gasoline vehicles and high particulate emissions from gasoline vehicles during cold start. These observations should be kept in mind when making recommendations to policymakers for urban air quality management.

Persons met

TERI is grateful to the following experts for the time spared by them for consultations and for the documents provided by them.

Dr D G Gajghate
Air Pollution Control Division
National Environmental Engineering Research Institute
Nehru Marg
Nagpur - 440 020
Phone: 226071, 221 523
Fax: 230 673
Email: apc@nagpur.dot.net.in

Dr M L Garg
Department of Biophysics
Panjab University
Chandigarh – 160 014
Email: mohan@pu.ac.in

Mr P Goyal
Air Pollution Control Division
National Environmental Engineering Research Institute
Nehru Marg
Nagpur - 440 020
Phone: 226071, 221 523
Fax: 230 673
Email: apc@nagpur.dot.net.in

Dr M Z Hasan
Air Pollution Control Division
National Environmental Engineering Research Institute
Nehru Marg
Nagpur - 440 020
Phone: 226071, 221 523
Fax: 230 673
Email: apc@nagpur.dot.net.in

Dr S K Jha
Environmental Assessment Division
Bhabha Atomic Research Centre

Mumbai – 400 085
Phone: 556 3140
Fax: 550 5151
Email: skjha@magnum.barc.ernet.in

Dr M Khare
Department of Civil Engineering
Indian Institute of Technology
New Delhi – 110 016

Dr A Vinod Kumar
Environmental Assessment Division
Bhabha Atomic Research Centre
Mumbai – 400 085
Phone: 556 3140
Fax: 550 5151
Email: avkumar@apsara.barc.ernet.in

Dr S D Makhijani
Central Pollution Control Board,
Parivesh Bhavan, East Arjun Nagar, Shahdra
Delhi - 110 032
Tele-fax: 222 0844

Dr M Mohan
Centre for Atmospheric Studies
Indian Institute of Technology
New Delhi – 110 016
Phone: 659 1313

Dr B S Negi
Environmental Assessment Division
Bhabha Atomic Research Centre
Mumbai – 400 085
Phone: 556 3140
Fax: 550 5151
Email: bsnegi@magnum.barc.ernet.in
Dr B Padmanabhamurthy
Consulting Engineering Services (India) Ltd.,
57, Nehru Place, (5th Floor)
New Delhi – 110 019

Phone: 648 5284

Fax: 646 0409

Prof R S Patil

Centre for Environmental Science and Engineering

Indian Institute of Technology

Mumbai – 400 076

Phone: 576 7858

Fax: 572 3480

Email: rspatil@cc.iitb.ac.in

Dr Rajendra Prasad

Envirotech Centre for Research and Development

A-271, Okhla Industrial Complex, Phase –1

New Delhi – 110 020

Phone: 681 4139, 681 3887

Fax: 681 1833

Email: envirotech@vsnl.com

Dr S Sadasivan

Environmental Assessment Division

Bhabha Atomic Research Centre

Mumbai – 400 085

Phone: 556 3140

Fax: 550 5151

Email: sada@magnum.barc.ernet.in

Dr I V Saradhi

Environmental Assessment Division

Bhabha Atomic Research Centre

Mumbai – 400 085

Phone: 556 3140

Fax: 550 5151

Email: ivs@magnum.barc.ernet.in

Dr V Sethi

Centre for Environmental Science and Engineering

Indian Institute of Technology

Mumbai – 400 076

Phone: 576 7809

Fax: 572 3480

Email: vsethi_india@hotmail.com

Dr J S Shahi
Department of Physics
Panjab University
Chandigarh – 160 014
Phone: 541 741
Fax: 783 336
Email: shahijs@yahoo.com

Prof. S S Srivastava
Department of Chemistry
Dayalbagh Educational Institute
Dayalbagh
Agra – 282 005
Phone: 281 545
Fax: 281 226
Email: sssdei@yahoo.com

Dr R M Tripathi
Environmental Assessment Division
Bhabha Atomic Research Centre
Mumbai – 400 085
Phone: 556 3142
Fax: 550 5151
Email: rmtripa@apsara.barc.ernet.in

Dr C Venkataraman
Centre for Environmental Science and Engineering
Indian Institute of Technology
Mumbai – 400 076
Phone: 576 7809
Fax: 572 3480
Email: chandra@cc.iitb.ac.in

Team members

- Dr Sumeet Saksena, Fellow
- Ms R Uma, Fellow
- Dr Nandini Kumar, Consultant

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Abbreviations and acronyms

AAS	Atomic absorption spectrophotometre
Al	Aluminium
AQCR	Air Quality Control Region
As	Arsenic
Ba	Barium
BaP	Benzo(a)pyrene
BC	Black carbon
BC _{water}	Black carbon soluble in water according to a technique used by the Max Planck Institute
Be	Beryllium
BghiP	Benzo(ghi)perylene
BIS	Bureau of Indian Standards
Br	Bromine
BSOM	Benzene soluble organic matter
BTX	Benzene, toluene and xylene
°C	Degrees celsius
Ca	Calcium
Ca ⁺²	Calcium ion
CALINE-3	California Line Source-3
CAMPS	Community Adoption and Monitoring Programme for Schools (conducted by TERI)
Ca _t	Calcium total (soluble and insoluble)
Cd	Cadmium
CDM	Climatological Dispersion Model
CH ₄	Methane
Cl	Chlorine
Cl ⁻¹	Chloride ion
CMB	Chemical mass balance
CO	Carbon monoxide
CPCB	Central Pollution Control Board
CPHERI	Central Public Health Engineering Research Institute
CPS	Cascade Particulate Sampler
Cr	Chromium
Cu	Copper

DMS	Dimethyl sulphide
EDXRF	Energy dispersive X-ray fluorescence
EGA	Evolved gas analysis
ESPs	Electrostatic precipitators
F ⁻¹	Fluoride ion
FA	Factor analysis
Fe	Iron
GC-FID	Gas chromatograph – flame ionisation detector
GEMS	Global Environmental Monitoring System
GNP	Gurunanak Public School (Teri monitoring site in Delhi)
GoI	Government of India
H	Hours
H ₂ S	Hydrogen sulphide
HC	Hydrocarbons
Hg	Mercury
HNO ₃	Nitric acid
HPLC	High performance liquid chromatography
HVS	High volume sampler
IAM	Intervention Analysis Model
IC	Ion chromatography
ICP	Inductively coupled plasma
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-ES	Inductively coupled plasma emission spectroscopy
IIT	Indian Institute of Technology
IITCO	Model developed by Indian Institute of Technology Delhi, Delhi for calculating CO concentration
IITLS	Indian Institute of Technology Line Source model
IITLT	Line Source model developed by IIT, Delhi
IMM	Intersection Midblock Model
INAA	Instrumental neutron activation analysis
INDOEX	Indian Ocean experiment
INDOEX-FFP	Indian Ocean experiment first field phase
INDOEX-IFP	Indian Ocean experiment intensive field phase
ISI	Indian Standard Institution
IT	Information technology
ITO	(Monitoring location near) the Income Tax Office, Delhi
JNU	Jawaharlal Nehru University (Teri monitoring site in Delhi)
K ⁺¹	Potassium ion

KTHM	Karmveer Ravsaheb Thorat Kala, Bhausaheb Higher Commerce and Annasaheb Murkute Science College
LPG	Liquefied petroleum gas
Mg	Magnesium
Mg ⁺²	Magnesium ion
MMAD	Mass median aerodynamic diameter
Mn	Manganese
Na	Sodium
Na ⁺¹	Sodium ion
NAAQMS	National Ambient Air Quality Monitoring Series
NAMP	National Ambient Air Quality Monitoring Programme
NDIR	Non-dispersive infrared
NEERI	National Environmental Engineering Research Institute
NGOs	Non-governmental organisations
NH ₃	Ammonia
NH ₄ ⁺¹	Ammonium (ion)
Ni	Nickel
NMVOC	Non-methane volatile organic compounds
NO	Nitric oxide
NO ₂	Nitrogen dioxide
NO ₃ ⁻¹	Nitrate (ion)
NO _x	Oxides of nitrogen
NPC	National Productivity Council
O ₃	Ozone
OC	Organic carbon
OH ⁻	Hydroxyl group
PAH	Polycyclic aromatic hydrocarbon
PAN	Peroxy acetyl nitrate
Pb	Lead
PCA	Principal component analysis
PEM	Pollution Episodic Model
PIXE	Proton induced X-ray emission
PM ₁₀	Particulate matter less than 10 microns
PM _{2.5}	Particulate matter less than 2.5 microns
PM ₂₅	Particulate matter less than 25 microns
QA/QC	Quality assurance / quality control
QCM-CI	Quartz crystal microbalance cascade impactor
Rb	Rubidium

Rs	Indian rupees
RSPM	Respirable suspended particulate matter
Sb	Antimony
Se	Selenium
SiO ₂	Silicon dioxide
SO ₂	Sulphur dioxide
SO ₄ ⁻²	Sulphate (ion)
SPCB	State Pollution Control Board
SPM	Suspended particulate matter
Sr	Strontium
TC	Total carbon
TERI	Tata Energy Research Institute
Ti	Titanium
TNMVOC	Total non-methane volatile organic compound
TSP	Total suspended particles
TSPM	Total suspended particulate matter
ULSM	Univariate linear stochastic model
UNEP	United Nations Environment Programme
URBAIR	Urban Air Quality Management Strategy in Asia
US EPA	United States Environmental Protection Agency
UV	Ultra violet
UV-VIS	Ultra-violet-visible
V	Vanadium
VOC	Volatile organic compound
WHO	World Health Organisation
WSOC	Water soluble organic carbon
Zn	Zinc
cm s ⁻¹	Centimetres per second
lpm	Litres per minute
mg m ⁻³	Milligrams per cubic metre
m ³ min ⁻¹	Cubic metre per minute
ng m ⁻³	Nanograms per cubic metre
Nm ³	Normal cubic metres
pH	A logarithmic scale for expressing the acidity or alkalinity of a solution, with 7 representing a neutral solution
ppbv	Parts per billion by volume
ppmv	Parts per million by volume

$\mu\text{g m}^{-3}$	Micrograms per cubic metre
μm	Micron, or 10^{-6} metre

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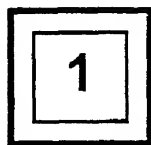
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Introduction

Background

Urban air quality is attracting increasing attention from policymakers, the Supreme Court, non-governmental organisations (NGOs), research institutions, universities, trade associations and donors in India. The majority of policy interventions to date, including recent important precedent-setting Supreme Court decisions in India, have focused on technical solutions for controlling emissions from road traffic. However, the actual contribution from road traffic is not known with any degree of certainty. Other significant sources of pollution, most notably small stationary sources, have not received much attention. As a result, it is almost certain that important emission sources and exposure pathways have been, and will continue to be, missed by the legislation if the current approach is not altered.

Scope of study

The objective of this assignment was to identify past and on-going work carried out in India that can be used to assess the contributions of different sources to urban air pollution (with a special focus on small particulate matter), and to pull together the existing knowledge to see what we can say with a reasonable degree of certainty, and what we do not yet know. Published papers and reports, conference proceedings, research reports, and university theses were among the sources of information. The information sought included the following.

- Air quality data collected using different techniques, especially those related to particles smaller than 10 or 2.5 microns (μm) in diameter ($\text{PM}_{10}/\text{PM}_{2.5}$), as opposed to total suspended particles (TSP), and any time-resolved data collected using automated systems.
- Emissions inventories and, where available, emission factors used to build the inventories.
- Dispersion modelling.
- Chemical analysis of TSP/ PM_{10} / $\text{PM}_{2.5}$.
- Source apportionment studies.

Once the data were gathered and relevant projects/studies identified, the study tried to assess the quality of the data or analysis where possible. For example, in the case of air quality data, how instruments are calibrated and how frequently may indicate if the data collected seem reasonable. In the case of emissions inventories, emission factors as well as sources considered give an indication of the comprehensiveness as well as the accuracy of the inventory.

Proposed methodology

The study was based essentially on a literature survey covering the following types of information sources:

- International peer-reviewed papers
- National peer-reviewed papers
- Central Pollution Control Board's (CPCB) National Ambient Air Quality Management System (NAAQMS) publications
- Research reports
- Student thesis.

The authors consulted other experts in the country extensively, through correspondence and in some cases through visits to their laboratories.

The specific issues considered under each objective were:

- Air quality
 - Indicative temporal and spatial trends, stratified across mega cities, metropolitan areas, and towns
 - Data quality issues
 - Representativeness of data (in terms of data accuracy and representativeness of monitoring sites)
 - Instrumentation
 - Correlations among pollutants
 - Primary and secondary pollutants
- Particulate characteristics
 - Size distribution
 - Choice of elements analysed
 - Analytical techniques
 - Carbon analysis
- Source apportionment studies
 - Types of models used

- Results
- Emission inventories
 - Fuel consumption data
 - Type of processes using fuels
 - Emission factors
 - Assumptions used
 - Spatial resolution
 - Matching of results with air quality data
 - Observations on the adequacy of inventories
- Air quality modelling
 - Types of models used
 - Data sources
 - Model validation

Based on the above review, this report summarises the state-of-the-art knowledge, and identifies (1) gaps in data and analysis, and (2) future needs.

Structure of the Report

This report begins by describing the National Ambient Air Quality Monitoring Programme in India and the results obtained in the programme as well as other studies examining three historically monitored pollutants, sulphur dioxide, nitrogen dioxide and total suspended particles. It then discusses studies measuring other pollutants in Chapter 3. Particulate matter is treated separately in Chapters 4 and 5 given its importance. Chapter 6 reviews emissions inventories and air quality modelling published to date. Chapter 7 concludes with recommendations arising from this review.

National Ambient Air Quality Monitoring Programme

The air quality monitoring programme in India was started in 1967 by the National Environmental Engineering Research Institute (NEERI) (then named CIPHERI, Central Public Health Engineering Research Institute). Monitoring was expanded to include regular monitoring at three stations in 1978. During 1984 and 1985, the Central Pollution Control Board (CPCB) established a network of seven monitoring stations for the National Ambient Air Quality Monitoring Programme (NAMP). This network has been expanded progressively and by March 1999, it comprised 290 stations covering over 90 towns and cities distributed over 24 states and 4 Union Territories. Of the 290 monitoring stations, which include 30 stations managed by NEERI, 204 stations are operating at present. In states such as Bihar, Haryana and Karnataka, fewer than 50% of the stations are in operation (CPCB 2000). The NAMP network is operated through the following agencies.

- Central Pollution Control Board, Headquarters, Zonal and Regional Offices
- State Pollution Control Boards (SPCBs) in respective states
- Pollution Control Committees in respective Union territories
- National Environmental Engineering Research Institute in 10 metro cities (NEERI 2001)
- Visveshwaraya Regional Engineering College, Nagpur and Pune (both in the state of Maharashtra)
- Pune University, Pune
- KTHM (Karmveer Ravsaheb Thorat Kala, Bhausaheb Higher Commerce and Annasaheb Murkute Science) College, Nasik in the city of Nasik (Maharashtra), and
- Walchand Institute of Technology, Solapur, in the city of Solapur (Maharashtra).

The pollutants that have been historically monitored regularly are sulphur dioxide (SO₂), nitrogen dioxide (NO₂) and suspended particulate matter (SPM). In addition to these three pollutants, NEERI monitors additional pollutants: ammonia (NH₃),

hydrogen sulphide (H₂S), respirable suspended particulate matter (RSPM) with an appropriate cut-off size of 10 µm and polycyclic aromatic hydrocarbons (PAHs). RSPM has also been recently added to the pollutants regularly monitored at many CPCB/SPCB monitoring stations. In Delhi, carbon monoxide (CO), ozone, benzene and trace elements have been monitored at a few locations by CPCB (<http://envfor.nic.in/cpcb/cpcb.html>). The Global Environment Monitoring System (GEMS) in India is supported by 30 monitoring stations operated by NEERI and the data are reported to CPCB, the United Nations Environment Programme (UNEP) and the World Health Organisation (WHO). Recently 8 new monitoring stations—two each in the states of Gujarat¹, Maharashtra, Tamil Nadu and Uttar Pradesh—were established under a World Bank project. The national ambient air quality standards are given in Table 2.1. The details of the regular monitoring programme are given in Table 2.2. Details of the monitoring techniques are provided in Table 2.3. The state-wise distribution of monitoring stations is presented in Map 2.1.

Table 2.1 National ambient air quality standards in India

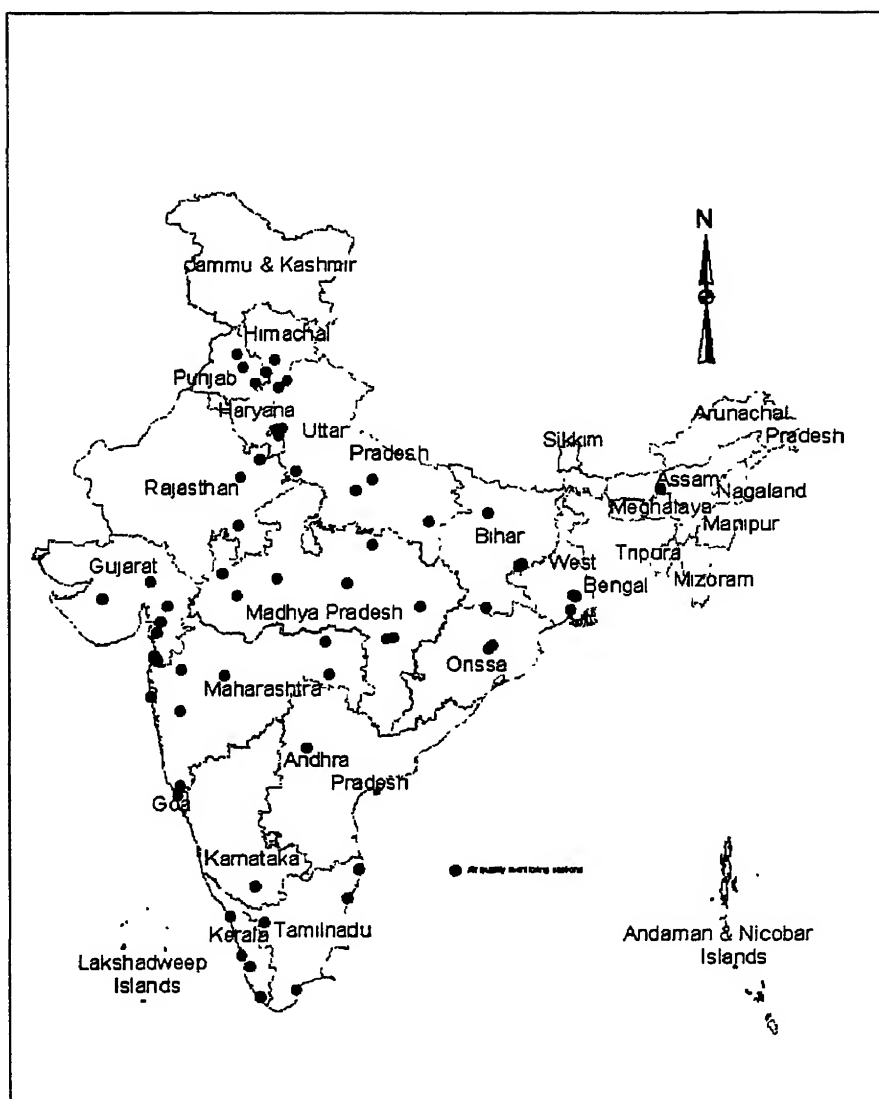
Pollutant	Time weighted average	Concentrations in ambient air		
		Sensitive areas (µg/m ³)	Industrial areas (µg/m ³)	Residential, rural and other areas (µg/m ³)
Sulphur dioxide (SO ₂)	Annual*	15	80	60
	24 hours**	30	120	80
Oxides of nitrogen as NO ₂	Annual*	15	80	60
	24 hours**	30	120	80
Suspended particulate matter (SPM)	Annual*	70	360	140
	24 hours**	100	500	200
Respirable particulate matter (RPM) smaller than 10 µm	Annual*	50	120	60
	24 hours**	75	150	100
Lead (Pb)	Annual*	0.50	1.0	0.75
	24 hours**	0.75	1.5	1.00
Carbon monoxide (CO)	8 hours**	1000	5000	2000
	1 hour	2000	10000	4000

* Annual arithmetic mean of minimum 104 24-hour measurements in a year taken twice a week at uniform intervals

** 24-hour/8-hour values should be met 98% of the time in a year. However, the standards may be exceeded 2% of the time but not on two consecutive days.

Source: CPCB 2000

¹ One at Ahmedabad has subsequently closed after the earthquake.



Map 2.1 Air monitoring stations in India

Table 2.2 Air quality monitoring programme in India

Monitoring agency	No. of locations	Cities	Programme	Sponsoring agencies	Parameters monitored	Remarks
NEERI	30 (3 each in 10 cities)	Ahmedabad, Mumbai,	NAMP,	CPCB,	RSPM, SO ₂ , NO ₂ ,	- The 30 stations are part of 290 stations supported by CPCB.
		Calcutta, Delhi,	GEMS	WHO &	NH ₃ , H ₂ S, SPM	- RSPM, NH ₃ , H ₂ S were introduced in 1990
		Hyderabad, Jaipur,		UNEP		- A few filters are being analysed for trace elements, PAH and ionic species.
		Kanpur, Kochi,				- SPM and RSPM were each monitored on 4 separate days in a month. Recently, however, they are being monitored simultaneously for 8 days.
		Chennai and Nagpur				- SO ₂ and NO ₂ are monitored for 6 days a month and NH ₃ and H ₂ S are monitored 2 days a month.
						- For the GEMS monitoring programme, NEERI does not receive funds from UNEP/WHO but the data are reported to UNEP/WHO.
CPCB/SPCB	260	90 cities/towns	NAMP	CPCB	SO ₂ , NO ₂ , SPM, RSPM	- RSPM monitoring was introduced in 1999 at 30 stations. By the end of 2000, 77 stations were monitoring RSPM.

Notes: Among the total 290 stations, 204 stations are in operation. In Delhi additional pollutants such as carbon monoxide, benzene, PAH, ozone, lead, cadmium and zinc are monitored at the ITO (Income Tax Office) station. Ahmedabad is in Gujarat, western India; Hyderabad is in Andhra Pradesh, southern India; Jaipur is in Rajasthan, northwestern India; Kanpur is in Uttar Pradesh, northern India; Kochi (formerly Cochin) is in Kerala, southern India; and Nagpur is in Maharashtra.

Table 2.3 Air quality monitoring techniques for various air pollutants

Air pollutants	Monitoring method	Principle	Measuring range	Sampling frequency, duration of sampling	Remarks
Sulphur dioxide (SO ₂)	Improved West and Gaeke method (sodium tetrachloro-mercurate method)	Absorption followed by colorimetric analysis	4 - 1050 µg m ⁻³	Twice a week - Daily average from six 4-hour samples	This method is for NO ₂ measurement, but NO gives positive interference. The Indian standards are for NO _x as NO ₂
Nitrogen dioxide (NO ₂)	Modified Jacob Hochrieser method (Sodium arsenite method)	Absorption followed by colorimetric analysis	3 - 420 µg m ⁻³	Twice a week - Daily average from six 4-hour samples	
Suspended Particulate Matter (SPM)	High volume sampling and gravimetric filter method	Sampling by high volume samplers with the average flow rate not less than 1.1 m ³ min ⁻¹	5 µg m ⁻³ - 10 000 µg m ⁻³ 0.3-100 µm particle size	Twice a week - Daily average from three 8-hour samples	Monitored only at NEERI monitoring stations
Respirable Suspended Particulate Matter (RSPM)	High volume sampling and gravimetric filter method	Sampling by RSPM sampler and cyclone size separation	5 µg m ⁻³ - 10 000 µg m ⁻³ 0.3 - 10 µm particle size	About 80 CPCB stations are monitoring RSPM. - Daily average from three 8-hour samples	
Ammonia (NH ₃)	Nessler's reagent	Absorption followed by colorimetric analysis		Twice a week - Daily average from six 4-hour samples	
Hydrogen Sulphide (H ₂ S)	Methylene blue	Absorption followed by colorimetric analysis		Twice a week - Daily average from three 8-hour samples	Not regularly monitored except at the ITO station in Delhi
Carbon monoxide (CO)	Automatic CO analyser	Non-dispersive infrared (NDIR) spectroscopy	0.1 ppmv - 10 ppmv	Continuous monitoring	

Regular monitoring programmes

Gas Chromatography with
flame ionisation detector
(GC-FID) GC-FID 0.3 - 100 ppmv

Notes: $\mu\text{g m}^{-3}$ micrograms per cubic metre; $\text{m}^3 \text{min}^{-1}$ cubic metres per minute; ppmv parts per million by volume

In the regular NAMP, the prescribed annual target sampling frequency is 104 days. But this target frequency has rarely been achieved at many monitoring locations. In certain states fewer than 50% of the stations are operational. As reported by CPCB (CPCB 2000), due to such problems as instrument failure, lack of trained manpower, and power failure, the target of 104 monitoring days per year is not achieved. In some locations the number of days on which air quality is monitored is fewer than 50 a year, which is considered inadequate for the purpose of data analysis. Until recently, RSPM was regularly monitored by NEERI 4 days a month and SPM was monitored 4 different days a month. Beginning in April 2001, simultaneous monitoring of SPM and RSPM is being gradually introduced at all the stations being operated by NEERI. In Delhi, gaseous pollutants are monitored by continuous automatic analysers by CPCB at two stations (ITO, near the Income Tax Office, and Siri Fort). SPM and RSPM are monitored every day of the year by the manual method (high volume sampling technique). In addition to the three historically monitored pollutants, CO and ozone (O_3) are monitored at ITO by CPCB.

Key findings from the NAMP

- The pollutant of concern in India, based on ambient concentrations recorded to date and known health effects, is SPM (which acts as a surrogate for smaller particles).
- Maximum SPM concentrations have been recorded at Kanpur, Calcutta and Delhi.
- Low SPM concentrations have been observed in south Indian cities such as Chennai, the capital of Tamil Nadu; Bangalore, the capital of Karnataka; and Hyderabad, the capital of Andhra Pradesh, in comparison with north Indian cities.
- Geographical differences in ambient SPM concentrations may be due to topography and weather conditions. In a paper published by Vishwanadham, Mishra and Satyanarayana (1995), the dilution capacity was reported to be high in southern parts of India and low in northern regions.
- The SO_2 concentrations are well within the national ambient air quality standards at many locations. High SO_2 levels have been recorded in Howrah (West Bengal), Calcutta and Pondicherry (a separate Union Territory in southern India) where the standards have been violated many times in the past.
 - The annual average concentrations of NO_2 have been well within the national ambient air quality standards, with the exception of non-compliance in some residential areas of Howrah, Vishakapatnam (Andhra Pradesh), and Kota (Rajasthan).

- The ambient concentrations of RSPM from 1998 to 1999 at ITO, which is a hotspot in Delhi, fluctuated between 56 micrograms per cubic metre ($\mu\text{g m}^{-3}$) and 820 $\mu\text{g m}^{-3}$.
- Ambient concentrations of RSPM and SPM monitored between March 1998 and December 1999 at the ITO crossing in Delhi showed that the percentage of RSPM in SPM varied between 34 to 69.
- The CO level at ITO, Delhi violates the national ambient air quality 8-hour standard of 2.0 milligrams per cubic metre (mg/m^3) most of the time. However, this standard is extremely stringent. Only on few occasions has the CO level exceeded the WHO health-based guideline of 10.0 mg/m^3 for 8 hours.
- Ozone concentrations averaged over an hour have been measured at ITO, Delhi since 1998 and the values have ranged between 26 and 104 $\mu\text{g m}^{-3}$, well within the standard set by the United States Environmental Protection Agency (US EPA) of 235 $\mu\text{g m}^{-3}$ and the WHO health-based guideline of 150 to 200 $\mu\text{g m}^{-3}$. Measuring ozone along a busy road is not meaningful, however, as ozone and its precursors may travel long distances and build up in suburban areas or long distances away from busy traffic corridors.
- The ambient concentrations of NH_3 in the winter of 1996 generally exceeded the 24 hour average standard of 400 $\mu\text{g m}^{-3}$ in Delhi and Calcutta. However, the annual average concentrations were within the standard of 100 $\mu\text{g m}^{-3}$ at both locations.
- The ambient concentrations of H_2S measured have been low at all of the 10 NEERI monitoring stations.

Quality assurance / quality control

Quality assurance and quality control (QA / QC) are vital components of air quality monitoring. QA / QC ensures that measurements are

- Representative of the ambient conditions
- Accurate and precise
- Reproducible
- Consistent over time (that is, settings do not drift)
- Able to achieve adequate data capture

In the NAMP, various agencies and organisations are involved. There appear to be no significant efforts towards quality control or cross-checking of the data generated by different agencies involved in the monitoring network. A CPCB report acknowledges that “the involvement of several agencies increase the probability of

variations and personal biases reflecting on the data. Therefore the air quality data statistics are indicative rather than absolute and perfect" (CPCB 2000).

As part of QA/QC procedures, the monitoring agencies are required to calibrate the samplers regularly for flow rate measurements, check the sampling train for leakage, select suitable filter papers and chemicals, and calibrate the colorimetre. But it is observed that these QA/QC measures are not followed rigorously in the field. To quantify the magnitude of errors, a review ("Review of GEMS air monitoring networks in operation in certain cities of South East Asia") was carried out by NEERI under the sponsorship of UNEP/WHO. In this programme parallel sampling and analysis was carried out in 5 cities. The instruments used in the parallel monitoring were centrally calibrated at Nagpur and checked against the practice followed in the field. The result showed a wide range of measurement errors in the selected cities (Table 2.4). The percentages in the table represent the differences in the values obtained between the two sets of instruments. In the larger network, which involves a number of institutions, the magnitude of errors is likely to be even greater than those indicated in Table 2.4.

Table 2.4 Integrated mean error in pollutant monitoring

City	Overall error range (%)		
	SPM	SO ₂	NO ₂
Bangalore	+8 to -25	+14 to -20	+14 to -19
Calcutta	-3 to -14	+24 to -37	+13 to -28
Chennai	+1 to +4	+22 to -31	+28 to -38
Delhi	-7 to -12	+16 to -27	+11 to -22
Mumbai	+17 to +26	+12 to -45	-3 to -30

Source: Unpublished report prepared for the review of GEMS air monitoring networks in operation in certain cities of South East Asia region

In the manual monitoring system (high volume sampling/gravimetric analysis and wet chemical methods), there are a number of reasons as to why the potential for significant errors exists.

Lack of skilled manpower

Experienced or well-trained staff are vital for the production of good quality data. The training of field assistants and other staff associated with data collection is a major requirement for generating data of adequate quality. Pollution control boards and other organisations manage the monitoring activities with limited manpower. The behaviour of field staff also plays a vital role in quality assurance measures. At many stations flow rates are not regularly calibrated. For the 24-hour monitoring of

particulate matter (SPM and RSPM), the filters have to be changed every 8 hours, and the absorbing tubes have to be changed every 4 hours for gaseous pollutants. The flow rates have to be recorded frequently. Some operators do not follow these protocols regularly. Having manuals and detailed site inspection records is also important. Occasional visits by the internal inspection team helps to check the operators' behaviour. This also greatly enhances the performance of the staff.

Financial support

The recruitment and retention of suitably qualified and self-motivated individuals requires considerably greater resources. Adequate resources are also necessary for the proper maintenance and calibration of the equipment. At one station, the allotted annual financial support for operation was only about Rs 100 000. This is grossly inadequate.

Data validation

Data validation enhances data integrity through the removal of spurious measurements produced by equipment malfunction, contamination or human error. This is a highly skilled procedure; it must be performed with considerable caution to ensure that invalidation of extreme but valid data does not occur. This requires time, experience and training but contributes to ensuring that data are valid and adequate for their intended use.

Representativeness of locations

The siting of a monitoring station is very important. It should be representative of the area selected. There should be free airflow (that is, tall buildings or trees should not obstruct the air flow). Ideally the sampler should be located four to twelve metres (m) above ground level. But due to such practical problems as lack of accessibility, lack availability of (reliable) power supply, and objections from residents to the noise created by the high volume air sampler, the criterion for sampling height is not satisfied at some locations where the samplers are placed 15 m above ground or even higher. Large height variation will in turn affect pollutant concentrations. In the absence of data from rural or background monitoring stations, the data obtained are not sufficient to differentiate between natural and anthropogenic source contributions.

Analytical methods

The present sampling and analysis techniques for gaseous pollutants also require special care. The modified Jacob and Hochheiser method is widely used for the

measurement of NO₂ in the ambient air. This method is reported to give 82% absorption efficiency for NO₂ in the concentration range from 40 to 750 µg m⁻³. This method is also sensitive to temperature, flow rate, and the type of bubbler. A study conducted at different flow rates ranging from 0.2 litres per minute (lpm) to 1.4 lpm using a standard bubbler showed an average collection efficiency of 87% at a flow rate of 0.2 lpm and a much reduced collection efficiency of 55% at a flow rate of 1.2 lpm (Goyal 1998). In India the flow rate varies from 0.2 to 1.5 lpm. In many cases the flow rate is not reported. Another paper (Goyal, Gavane and Aggarwal 2000) reported the impact of temperature on the absorbing efficiency. The maximum absorbing efficiency of 88% was recorded at a temperature of 26°C. At lower and higher temperatures the absorbing efficiency was lower. At 16°C and 36°C, for example, the average absorption efficiency was 85% and 78%, respectively. The temperature variations in India are large (less than 5°C in winter to 45°C or even higher in summer). Therefore the temperature during sampling should be maintained constant, for example by keeping the sampling train in ice. Otherwise a suitable correction factor should be applied during data reduction.

The present RSPM monitoring has cyclone-based separation attached to the high volume air sampler. The commonly used equipment for RSPM monitoring is the respirable dust sampler supplied by Envirotech Instruments Private Limited. The know-how was developed by NEERI. The cyclone separation is designed to provide a cut-off at 10 µm (quoted by the manufacturer). But as a centrifugal separation system, this cut-off is bound to vary with the nature and density of dust particles. The system has been tested extensively by NEERI for a variety of particles such as coal dust, cement and fly ash. Table 2.5 provides a summary of the results of these tests.

Table 2.5 Particle size cut-off for the cyclone-based RSPM sampler

Nature of dust	Specific gravity	Collection size (µm)
Coal	1.4-1.8	10-12
Road-side dust	2.0-2.2	8-10
Fly ash	2.3-2.4	7.5-9
General mining (limestone / sandstone)	2.5-2.7	7-9
Cement	3-3.3	6-8
Manganese ore	3.5-4	5-7

Source: Envirotech, respirable dust sampler manual

Other studies

In addition to the NAMP, air quality is also monitored by CPCB at various traffic intersections using a mobile van in Delhi. A few research institutes, NGOs, and others are also involved in monitoring. In Delhi, Tata Energy Research Institute (TERI) has

been monitoring RSPM, SO₂, and NO₂ at Lodi road since 1998. Between July 2000 and July 2001, TERI monitored air quality at ten additional locations in Delhi as part of the Community Adoption and Monitoring Programme for Schools (CAMPS, programme description and data available at www.teriin.org/camps/envdata.htm#monitor). The Eureka Forbes Institute of Environment regularly monitors air quality at one station in each of the ten metro cities.

Key findings from the TERI monitoring programme

- RSPM concentrations violated the national ambient air quality standards for most of the monitored period.
- RSPM concentrations were low in the monsoon period.
- The daily average RSPM concentrations of as high as 600 $\mu\text{g m}^{-3}$ were recorded during the months of May and June 2001 when dust storms were observed.
- On the Diwali day, the RSPM concentrations at night (22:00 to 06:00) exceed 1500 $\mu\text{g m}^{-3}$ at all the monitoring locations.
- SO₂ concentrations were well within the national ambient air quality standards for all the days monitored. Most of the daily average values were less than 30 $\mu\text{g m}^{-3}$.
- Monthly average NO₂ concentrations varied from 20 $\mu\text{g m}^{-3}$ to 120 $\mu\text{g m}^{-3}$.
- Very high RSPM values were recorded in Harinagar which is a residential area.
- An overall difference of about 52% in RSPM concentrations was found when filters were collected at two different heights of approximately 4 m and 14 m at the Harinagar monitoring station. This finding may be site-specific. More detailed analysis at different heights at other locations is needed.
- No significant differences in the gaseous pollutant levels were observed at different heights.
- A study was conducted by TERI during the months of December 1999 and January 2000, in an office building located near ITO, Delhi. The SPM and RSPM levels were monitored at two different heights, 4 m and 14 m above ground level (TERI 2000). The percentage of RSPM in SPM was 50 to 70 at 4 m, and 40 to 60 at 14 m. A comparison of measured concentrations is given in Table 2.6.

Table 2.6 Concentration of SPM and RSPM at two different heights at an office building near ITO, Delhi

Date	Sampling at the height of 14 m			Sampling at the height of 4 m		
	SPM ($\mu\text{g m}^{-3}$)	RSPM ($\mu\text{g m}^{-3}$)	RSPM/SPM (%)	SPM ($\mu\text{g m}^{-3}$)	RSPM ($\mu\text{g m}^{-3}$)	RSPM/SPM (%)
13.12.99	459	202	44	503	280	56
17.12.99	—	250	—	520	283	54
20.12.99	499	218	44	481	255	53
03.01.00	502	309	62	591	357	60
07.01.00	584	343	59	618	378	61
10.01.00	548	332	61	603	371	62
14.01.00	407	211	52	361	250	70
17.01.00	308	132	43	—	220	—
Average	475	258		498	305	

Note RSPM concentrations measured at 4 m were markedly higher than those at 14 m. While RSPM concentrations generally decline with increasing height, the magnitude of the difference may be site-specific.

Source: TERI 2000

Examples of other studies conducted on three historically monitored pollutants are shown in Table 2.7.

Table 2.7 Summary of concentrations of historically monitored pollutants reported in other studies

City	Type of site	Year	Pollutant	Analytical technique	Source	Key findings
Delhi	Traffic intersections	1997	SPM,	SPM – High volume sampler	CPCB 1999a	- SPM and RSPM generally exceeded the limit at all stations.
			RSPM,	RSPM – Cyclone based high volume sampler		- All SO ₂ values were well within the national standards.
			SO ₂ , NO ₂ , O ₃ , Pb,	SO ₂ , NO ₂ , O ₃ – Absorption followed by chemical analysis		- The mean 24 h NO ₂ concentrations exceeded the national standard at 8 out of 18 locations.
			PAH	Pb – AAS PAH – GC/FID Sampling period was 24 hours		- For lead, ozone and PAH, see Table 3.1.
Delhi	Traffic intersections	1999	SPM,	SO ₂ , NO ₂ , CO – automatic analyser	CPCB 1999b	- Annual average NO ₂ concentrations were lower than in 1995 by 3% to 7%
			SO ₂ , NO ₂ , CO, Pb	SPM – High volume sampler Pb – AAS		- Annual average SO ₂ concentrations at traffic intersections were lower by 20% than in 1999
						- For lead, see Table 3.1.
Delhi	Residential and Industrial	1998	SPM,	SPM – High volume sampler	Gowda et al. 2000	- The 24 hour (h) mean SO ₂ concentration varied from 6 to 22 µg m ⁻³
			RSPM,	RSPM – Cyclone based high volume sampler		- * The daily mean NO ₂ concentration for the winter season exceeded the standard at 4 out of 11 monitoring stations. The daily average values were not cited in this article.
			SO ₂ , NO ₂	SO ₂ , NO ₂ , O ₃ – Absorption followed by chemical analysis Sampling period of 24 hours		- * The daily mean SPM concentration ranged from 361 to 838 µg m ⁻³
						- The daily mean RSPM concentration for the winter season exceeded the standard at all the monitoring stations
Calcutta	19 Traffic intersections	1995 -	NO _x	A set of 3 passive samplers exposed for a period of 14 days at a time over a year	Mondal et al. 2000	- NO _x concentration ranged from 55 µg m ⁻³ (peak monsoon) to 222 µg m ⁻³ (winter)
		1996	(oxides of nitrogen)			- Background NO _x concentration was 11 µg m ⁻³
Mumbai	Traffic	1997	NO _x	Automatic analyser	Lal and Patil	- 24 h mean NO _x concentration of exceeded the standard of 80 µg m ⁻³

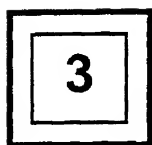
City	Type of site	Year	Pollutant	Analytical technique	Source	Key findings
	intersection				2001	<ul style="list-style-type: none"> - The concentration of NO, NO₂ and NO_x showed a bimodal temporal distribution with a peak during 8:00 – 10:00 and 19:00 – 21:00 - The spatial variation showed that NO concentration decreased with increasing distance from the road but NO₂ concentration remained the same
Agra (in Uttara Pradesh, close to Delhi)	Residential, commercial and near highway	1991 - 1992	SO ₂ and sulphate (SO ₄ ⁻²)	SO ₂ – Absorption followed by chemical analysis Sulphate – Ion chromatograph	Parmar <i>et al.</i> 1999	<ul style="list-style-type: none"> - 24 h SO₂ concentration varied between 6.3 and 20.4 µg m⁻³ while SO₄⁻² concentration varied between 23.3 and 64.8 µg m⁻³ - Alkaline dust particle and metal ions seemed to play a catalytic role in the oxidation of SO₂ to sulphate
Indore, Madhya Pradesh	Residential, Industrial and roadside	1985 - 1987	SO ₂	SO ₂ concentrations computed from sulphating rates measured by exposing lead candles	Joshi, Pawar and Wagela 1993	<ul style="list-style-type: none"> - Annual SO₂ concentration varied from 18 µg m⁻³ to 80 µg m⁻³ - The impact of SO₂ on five tree species was studied; among the test tree species <i>E. Jambolana</i> planted near a textile mill recorded the lowest pH of 4.9 whereas the <i>Eucalyptus</i> species were least affected - The sampling and analytical method is not the standard recommended procedure, and hence it is possible that there large errors associated with the reported values
Mysore, Karnataka	Industrial and residential area	1997	SPM, SO ₂ , NO ₂	SPM – High volume sampler SO ₂ , NO ₂ – Absorption followed by chemical analysis	Hosamani and Doddamani 1998	<ul style="list-style-type: none"> - 8 hour average concentrations of SO₂ and NO₂ were well within the national standards - In two commercial areas the 8 h mean SPM concentrations were higher than 80 µg m⁻³ - Avenue trees in these areas developed dark patches. The authors attributed this to chlorosis caused by NO₂. However, NO₂ concentrations were below 40 µg m⁻³, well within the air quality standards. Further, chlorosis is yellowing of leaves and not development of dark patches.

* The monitoring was carried out for one season and the data collected were compared with 24 hour average for indicative purposes.

Notes: AAS atomic absorption spectrophotometry, Pb lead

Summary

- A study by CPCB at a traffic intersection in Delhi indicated that the percentage of RSPM in SPM varied from 34 to 69% (CPCB 2000).
- Although the BIS (Bureau of Indian Standards) guidelines prescribe the sampling height of 4 m to 14 m from ground level (ISI 1986), this requirement is not met at many locations due to such limitations as lack of accessibility, lack of reliable power supply, surrounding tall buildings and objections from the nearby residents to high noise levels caused by high volume samplers. At many locations, the sample inlet is located 15 m above ground level or higher.
- A study by TERI indicates that there are significant variations in the ratio of RSPM to SPM as well as absolute concentrations with sampling height.
- Generally information on background particulate concentrations is not available, as there is no monitoring in rural areas under NAMP.
- NO₂ concentrations reported by various agencies vary significantly. This indicates a lack of adequate QA/QC. The present active sampling and analysis methods are sensitive to such parameters as temperature, sample flow rate, and the type of absorber used. A suitable correction factor, therefore, must be applied to estimate actual NO₂ concentrations in the ambient air using the arsenite method in South Asia where atmospheric temperature variations are large.



Other pollutants

Besides the three pollutants that have been historically monitored, a number of other pollutants are more important from the point of view of public health. Some of the studies covering other pollutants—lead, non-methane hydrocarbons (NMHCs), ozone, CO, methane, benzene and PAH—are listed in Table 3.1. Lead is further discussed in Chapter 4. Respirable and fine particulate matter, because of their importance, are treated separately in Chapters 4 and 5. Ozone, VOCs, PAHCs, ammonia and sulphates are discussed below.

Ozone

A two-year study at fifteen locations (samplers at a height of 2.5 m above ground) in Varanasi in Uttar Pradesh (Pandey and Agrawal 1994) indicated that ozone concentrations peaked from late morning to afternoon in summer and those of SO₂ and NO₂ during early morning and late evening in winter. They observed that upwind sites had lower levels of pollution. Seasonal and diurnal variations in pollutant concentration could be attributed to the meteorological variations and partially to the timing and nature of emissions. Low temperature and calm conditions during winter contributed to the elevated levels of SO₂ and NO₂. Significant negative correlations were observed between monthly average concentrations of SO₂ and NO₂ and the mean monthly temperature. Concurrent formation of inversion layers further contributed to the overlaps of concentration peaks of these two pollutants during the morning and evening hours. Asynchrony in the concentration peaks of NO₂ and O₃ suggested the atmospheric transformation of the former into the latter. Further, ozone, a secondary pollutant, is very much dependent on the intensity of solar radiation and air temperature. Significant positive correlations between the mean monthly temperature and monthly average concentrations of ozone indicated temperature-dependent oxidant formation resulting in ozone concentration maxima in the afternoon.

Table 3.1 Summary of measurements of other pollutants

City	Pollutant	Year of monitoring	Type of site	Method of sampling and analysis	Key findings	Reference	Remarks
Delhi	Lead	1992	Traffic intersections	Atomic absorption spectrophotometre (AAS)	<ul style="list-style-type: none"> - The 24 hour (h) standard of $1.0 \mu\text{g m}^{-3}$ was exceeded at most locations - Highest value of $8.5 \mu\text{g m}^{-3}$ was observed in Shahadara 	CPCB 1999a	- Unleaded gasoline was in use
Delhi	Lead	1997	Traffic intersections	AAS	<ul style="list-style-type: none"> - 24 h average value varied from $0.2 \mu\text{g m}^{-3}$ to $2.6 \mu\text{g m}^{-3}$ - Lead levels at 6 out of 19 locations exceeded the 24 h standard - Highest values were found at night rather than in the morning or during the day 	CPCB 1999a	- From 1994 the Lead content in the gasoline was reduced from 0.56 g/l to 0.15 g/l
Delhi	Lead	1999	Traffic intersections	AAS	<ul style="list-style-type: none"> - 24 h average varied from $0.05 \mu\text{g m}^{-3}$ to $0.08 \mu\text{g m}^{-3}$ - The lead level was reduced by 49% compared to 1999, and by 79% compared to 1995 	CPCB 1999b	- Unleaded gasoline was in use
10 cities in India	Lead	1991	Residential & industrial area	AAS	<ul style="list-style-type: none"> - Mean daily lead levels varied from 0.009 to $2.3 \mu\text{g m}^{-3}$ - High lead concentrations were recorded in Mumbai, Calcutta and Delhi 	Gadhate and Hasan 1999	
Varanasi	Lead	1988 - 1989	Urban area	AAS	<ul style="list-style-type: none"> - 24 h mean concentration varied from 0.01 - $0.78 \mu\text{g m}^{-3}$ - Higher 24 h mean concentrations were 	Tripathi 1994	- Leaded gasoline was in use

City	Pollutant	Year of monitoring	Type of site	Method of sampling and analysis	Key findings	Reference	Remarks
Lucknow, Uttar Pradesh	Lead	1993	Traffic intersection	AAS	- Highest concentration of $2.96 \mu\text{g m}^{-3}$ was observed near road side - Concentration decreased with increasing distance from road	N. Singh <i>et al.</i> 1995	observed near highway and traffic junctions
Delhi	NMHC	1994-1995	Urban areas	GC-FID	- Daily concentration of grab samples ranged from 1.3 to 32.5 ppmv - Peak values were observed during peak traffic hours	Padhy and Varshney 2000	
Mumbai	NMHC	1993-1994	Industrial location	GC-FID	- 44 to 50% of the samples violated the standard set for zones with chemical industries by the Maharashtra Pollution Control Board of 240 ppbv.	Mohan Rao <i>et al.</i> 1997	
Delhi	Ozone	1993	Residential	Absorption followed by colorimetric analysis	- Ozone concentration varied from 34 to 126 ppbv - High levels were observed during morning hours - Delayed build-up of ozone in the evening	A. Singh <i>et al.</i> 1997	
Delhi	Ozone	1997	Traffic intersections	Absorption followed by chemical analysis	- Detectable only at 7 locations	CPCB 1999a	
Delhi	Ozone	1998-1999	Traffic intersection	Absorption followed by colorimetric analysis	- Hourly average concentration varies from $26 \mu\text{g m}^{-3}$ to $104 \mu\text{g m}^{-3}$	CPCB 2000	

City	Pollutant	Year of monitoring	Type of site	Method of sampling and analysis	Key findings	Reference	Remarks
Varanasi	Ozone	1989		Absorption followed by colorimetric analysis	- Maximum hourly concentration of 160 $\mu\text{g m}^{-3}$ was observed in summer	Pandey <i>et al.</i> 1992	
Delhi	Ozone	1989-1990	Urban area	Absorption followed by colorimetric analysis	- Hourly values varied from 9.4 to 128 ppbv - Peak hourly values were observed during early summer and spring	Varshney and Aggarwal 1992	
Delhi	Ozone and NO_2	1982-1987	Urban area	Absorption followed by colorimetric analysis	- Mean hourly concentration of ozone decreased progressively from winter (68.4 $\mu\text{g m}^{-3}$) to monsoon (28.6 $\mu\text{g m}^{-3}$) - Overall mean concentration averaged from December 1982 to March 1987 was 57.5 $\mu\text{g m}^{-3}$ - Mean 2 h concentration of O_3 increased from 38.4 $\mu\text{g m}^{-3}$ in 1983 to the 104.2 $\mu\text{g m}^{-3}$ in 1986 - Mean annual NO_2 concentration was less than 5.0 $\mu\text{g m}^{-3}$	Kapoor <i>et al.</i> 1990/91	- Measurements were carried out for more than 500 days over a period of 5 years - Samples were collected for a period of 2 hours at a time - NO_2 concentrations were found to be very low, possibly due to the sampling location or measurement error
Delhi	Ozone, NO and NO_2	1995-1996	Residential	Absorption followed by colorimetric analysis	- The mean concentration of ozone (average for a period of 3 months) varied from 21.8 ppbv to 49.6 ppbv	Kulshrestha, Jain, Parashar 1997	- Ozone samples were collected at two different heights, 13 m and 30 m above the ground. - Sampling was carried out for a period 30 minutes but the measurements were quoted as hourly data, which is not a true representation - The study does not report the sample

City	Pollutant	Year of monitoring	Type of site	Method of sampling and analysis	Key findings	Reference	Remarks
Ahmedabad, Gujarat	Ozone, NO _x , CO and methane (CH ₄)	1993-1996	Urban area	Ozone by UV NO _x by chemiluminescence CO and CH ₄ by GC/FID	<ul style="list-style-type: none"> - Hourly ozone concentration increased from the night time base value of 14 ppbv to 34 ppbv during the day time - High concentrations of ozone and precursor gases during autumn and winter with the transition period from September to October in spite of lower solar radiation. This is due to higher levels of precursors, large scale transportation and lower boundary height (see text) - Both NO_x and CO levels were high during the morning and late evening period - Lowest NO_x and CO concentrations were observed during 14:00 – 17:00 in all the months 	Lal, Naja and Subbaraya 2000	<ul style="list-style-type: none"> - Simultaneous measurements of ozone and its precursors were carried out with automatic samplers. Diurnal and seasonal variations were also studied
					<ul style="list-style-type: none"> - Mean 2-hour O₃ and NO₂ concentrations were 39.4 µg m⁻³ and 40 µg m⁻³, respectively - O₃ concentrations were positively correlated with temperature and negatively correlated with humidity - NO₂ concentrations were inversely correlated with temperature and 		
Agra	Ozone and NO ₂	1994 - 1996	Suburban area	Absorption followed by colorimetric analysis	<ul style="list-style-type: none"> - Mean 2-hour O₃ and NO₂ concentrations were 39.4 µg m⁻³ and 40 µg m⁻³, respectively - O₃ concentrations were positively correlated with temperature and negatively correlated with humidity - NO₂ concentrations were inversely correlated with temperature and 	Khare <i>et al.</i> 1997a	<ul style="list-style-type: none"> - 182 samples were collected for a period of 2 hours during the period May-June 1995 and 1996, December 1994, and February 1995

Other pollutants

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City	Pollutant	Year of monitoring	Type of site	Method of sampling and analysis	Key findings	Reference	Remarks
Chandigarh (Union Territory in northern India)	Ozone	1984, 1990 - 1991	Urban area	Passive ozone analyser	- Values were identical in 2 time frames - Monthly average ranged from 26 to 55 ppbv	Bhatnagar, Srinivas and Sangeeta 1992	
Delhi	Benzene	1998	Various locations	Passive adsorption followed by GC-FID,	- 88 $\mu\text{g m}^{-3}$ at residential area - 42 – 195 $\mu\text{g m}^{-3}$ at traffic intersections - 164 – 182 $\mu\text{g m}^{-3}$ at petrol pumps	CPCB 2000	- After phasing out of lead, the amount of benzene in gasoline likely increased
Mumbai	Benzene	1993 - 1994	Industrial area	GC/FID	- Concentrations exceeded 16 $\mu\text{g m}^{-3}$ at 4 out of 5 locations	Mohan Rao et al. 1997	- Samples collected for 3 h at a time
Delhi and Mumbai	PAH	1992	Urban area	GC/FID	- 150-750 ng m^{-3} in Mumbai - 30 - 750 ng m^{-3} in Delhi	Agarwal (unpublished paper)	- Samples were collected at various times during 1992
Delhi	PAH	1997	Traffic intersections	GC/FID	- Fluoranthene and benzanthrane were the dominant compounds in SPM and RSPM	CPCB 1999a	
Delhi	PAH	1998	Residential & Industrial area	GC/FID	- Winter - 30.3 - 60.9 ng m^{-3} - Summer - 16.0 - 29.3 ng m^{-3} - Monsoon - 9.4 - 27.8 ng m^{-3}	CPCB 2000	

* Ten locations in India = Delhi, Kanpur (Uttar Pradesh), Ahmedabad (Gujarat), Mumbai, Cochin (Kerala), Calcutta, Hyderabad (Andhra Pradesh), Nagpur (Maharashtra) and Chennai

Note: ng m^{-3} nanograms per cubic metre; NMVOC non-methane volatile organic compounds.

Another study by Pandey and Agrawal (1992) in Varanasi reported seasonal and diurnal variations in the ambient air concentrations of ozone in Varanasi city, India for the years 1989 and 1990. Different monitoring zones were established in the city on the basis of pollution sources, traffic densities, and structure of built-up areas. At most of the monitoring stations, 2-hour ozone concentrations frequently exceeded $60 \mu\text{g m}^{-3}$ (30 ppbv, parts per billion by volume) during summer months. However, the zone dominated by residential colonies, offices, and cultivated land showed maximum O_3 concentrations less than $60 \mu\text{g m}^{-3}$ (30 ppbv). Higher concentrations of ozone were recorded mainly in warmer months between 11 am to 4 pm. The highest 2-hour mean O_3 concentration of $160 \mu\text{g m}^{-3}$ (80 ppbv) was recorded in the month of April at Zone I. Monthly average ozone concentrations were significantly correlated with temperature (correlation coefficient $r = 0.69$), relative humidity ($r = -0.81$), wind speed ($r = 0.76$), and atmospheric pressure ($r = -0.46$).

Measurements of ozone in the urban environment of Delhi were carried out at ground level and heights of 23 m, 51 m, 117 m and 153 m at four different sites synoptically during 1989-90 (Varshney and Aggarwal 1993). A considerable ozone build-up and significant vertical variations in concentration were observed all over Delhi. At any given time, O_3 concentrations were lowest at ground level and invariably increased with increasing distance from the ground.

Measurements of ozone and oxides of nitrogen (NO_x) were carried out at six sites in Delhi during the winter months of 1993 (A. Singh *et al.* 1997). Concentrations of ozone and NO_x varied between 34 ppbv ($67 \mu\text{g m}^{-3}$) and 126 ppbv ($247 \mu\text{g m}^{-3}$) and between 32 ppbv ($60 \mu\text{g m}^{-3}$) and 272 ppbv ($512 \mu\text{g m}^{-3}$), respectively. Interestingly, ozone exhibited initial high levels during morning hours, subsequently declining to lower levels by noon. However, during evening hours a delayed build-up of ozone was observed which is a departure from earlier studies. The micro-meteorological parameters like the mixing height, greater in the late evening, and ventilation coefficient, again greater in the late evening, were observed to favour dispersion of the pollutants, predominantly between 11:00 and 18:00, whereas stable atmospheric conditions between late evenings to early morning hours seemed to favour accumulation of the pollutants. The paper reported some unusual winter diurnal ozone trends and speculated the possible reasons.

Surface measurements of ozone, NO_x , CO and methane (CH_4) have been made over an urban site, Ahmedabad (23°N , 72.6°E) in tropical India (Lal, Naja, and Subbaraya 2000). Ozone concentrations were measured during in the period 1991-1995; NO_x , CO and CH_4 concentrations were monitored during the period 1993-1996. Ozone, NO_x and CO showed diurnal variations typical of an urban site. However, high concentrations of ozone, exceeding 80 ppbv ($157 \mu\text{g m}^{-3}$), were rarely observed.

The day time ozone production is basically due to the photo-oxidation of its precursor gases. During the day, the average concentration of ozone increased from the night time base value of about 14 ± 2 ppbv ($28 \pm 4 \mu\text{g m}^{-3}$) to 34 ± 9 ppbv ($67 \pm 18 \mu\text{g m}^{-3}$). However, its diurnal amplitude varies during different months. Diurnal variations in NO_x and CO are a manifestation of combined effects of local emissions, boundary layer processes, atmospheric chemistry and local wind pattern. Ozone concentrations were observed to be maximum during autumn and winter months due to higher amounts of precursor gases, in spite of lower solar radiation. Higher concentrations of precursors during autumn and winter are due to large scale transportation from the continent and lower boundary layer heights. Contrary to the seasonal variation, the diurnal variation of precursor gases was negatively correlated with that of ozone.

Summary

- Only a limited amount of data is available for ambient concentrations of ozone in India. Measured ozone concentrations have generally been found to be low in Indian cities to date. In the studies measuring ozone, it appears that non have corrected for the impact of temperature on measurements, compromising data quality.
- Many studies measuring ozone concentrations have tended to focus on traffic intersections, such as ITO junction in Delhi. Since ozone and its precursors travel large distances, it is important to measure ozone away from traffic corridors. Ozone concentrations may very well be much higher in non-traffic areas.
- Care should be taken during sampling and colorimetric analysis (which is the most widely used analytical method). In this method potassium iodide is used as the absorbing reagent and the amount of iodide released is measured. High temperature may also release iodine. The samples should be analysed immediately.
- Of all the pollutants measured, ozone appears to show the most distinct diurnal variation that in turn seems to be closely associated with traffic.

Volatile organic compounds (VOCs)

Studies on non-methane volatile organic compounds (NMVOCs) have included measurements of the following classes of compounds: alkanes, alkenes, aromatics, alcohols, terpenes, carbonyl compounds (specially formaldehyde) and carboxylic acids.

The emissions of biogenic (*viz.*, of natural origin) volatile organic compounds exceed those from anthropogenic sources by an order of magnitude. NMVOCs have a

significant impact on photochemical processes that lead to the formation of ozone (a secondary pollutant) and other photo-oxidants including tropospheric ozone and peroxyacetyl nitrate (PAN). These are injurious to health and highly phytotoxic; some NMVOCs are even carcinogenic. Few Indian studies cover measurements of the above-mentioned compounds. Available reports give estimates of formaldehyde (Khare *et al.* 1997b, 1997c, 1998a, 1998b), acetic and formic acids (for example, see Kumar *et al.* 1993a, 1993b, 1996) in particulate matter, dustfall², rainwater and the vapour phase. However, in contrast to most work reported from developed countries, no attempts have been made to draw up inventories of the sources, natural or anthropogenic, in India. The absence of source inventories in turn precludes the possibility of formulating budgets (sources and sinks) for critical species.

A team in Dayalbagh, Agra, studied organic acids (formic and acetic) and formaldehyde at a suburban site as well as a rural area selected to represent background concentrations (Kumar *et al.* 1993a, 1993b, 1996). The levels of formic and acetic acid in the vapour phase reported were not widely different from those at similar sites in other parts of the world. In the study reporting vapour phase formaldehyde in the monsoon (Khare *et al.* 1997b, 1997c), formic and acetic acids correlated well with each other but poorly with formaldehyde, suggesting that both acids were probably emitted directly by natural sources rather than formed by photochemical reactions.

In Delhi, NMVOCs have been reported by a group at the Jawaharlal Nehru University (Padhy and Varshney 2000, Varshney and Padhy 1998). Both studies covered thirteen sites in Delhi with varying traffic characteristics and explained the observed concentrations on the basis of traffic density without correlating with precursor gases and carrying out other types of analysis. Diurnal and seasonal variations were attributed to solar insolation and weather conditions. The results showed that ambient NMVOC concentrations in Delhi varied between 1.3 and 32.5 ppmv, exhibiting wide temporal and seasonal variation. NMVOC concentrations peaked mostly at 09:00, which coincided with the peak traffic hour. The measurements were carried out by trapping air in hypodermic syringes and analysing using GC-FID. However, the authors did not determine if temporal and spatial differences were statistically significant. This lack of statistical analysis makes conclusions drawn about the sources of emissions less certain.

² Dustfall can be defined as particulate material deposited by sedimentation and impaction on a surface along with gaseous compounds. Dustfall is of interest as a lower limit of the dry deposition on a given surface.

Another study of non-methane hydrocarbons was carried out in Mumbai (Mohan Rao *et al.* 1997). The study had a sample size of 260, collected over a period of 14 months. Although the study did not aim to apportion sources, levels of C₂-C₅ hydrocarbons (hydrocarbons with two to five carbon atoms) were greater than those of C₆-C₁₀ in the vicinity of a refinery. In this study, benzene concentrations were greater than 5 ppb (16 µg m⁻³) and the authors pointed out that no air quality standards for organic contaminants had been set in India. They also recommend principal component analysis (PCA) be used to establish the relative contributions of different hydrocarbon sources. A comparison of hydrocarbon-to-acetylene and benzene-to-toluene ratios confirmed that emissions from industries were more important than automobiles at this site.

Measurements of C₂-C₅ hydrocarbon concentrations in Deonar, Bombay (now Mumbai) were reported by Pandit and Mohan Rao (1990). The auto exhaust emissions of C₂-C₅ hydrocarbons from some gasoline-fuelled vehicles in Mumbai were also measured. The auto exhaust contribution to atmospheric C₂-C₅ hydrocarbons was evaluated by a comparison of the ratios of ambient concentrations of individual hydrocarbons to acetylene and auto exhaust samples. About 10% of the C₂-C₅ hydrocarbons in the Deonar region were calculated to be due to auto exhaust emissions. Only a small amount (1.2%) of the isobutane was from auto exhausts while a large fraction was attributed to possible emissions from refinery operations in the region.

The concentrations of benzene, toluene and xylene (BTX) were measured over a period of three years by a group at the JadHAVpur University, Calcutta (Samanta *et al.* 1998). Gas chromatography (GC) with a flame ionisation detector (FID) was used to analyse the samples. The authors sampled aromatic concentrations in winter in Calcutta for three years, 1992, 1993, and 1994. Xylene levels were reported to range between 60 and 120 µg m⁻³, toluene between about 100 and 1200 µg m⁻³, and benzene between 1,000 and 8,000 µg m⁻³. The authors were unable to explain the high measured concentrations of benzene and toluene, one or two orders of magnitude higher than those measured elsewhere. This group also estimated some benzene soluble organic matter (BSOM, extracted in benzene using a soxhlet extractor) and PAHs in SPM (extracted from the BSOM, analysed using high pressure liquid chromatography, HPLC). The mean BSOM values for 5 stations varied from 71 µg/m³ to 160 µg/m³. Although source apportionment was not a specific aim of the study, some efforts were made to explain the observed levels based on traffic density (and hence automotive exhaust), kerosene and coal-burning. In 1996, the same group measured BTX in and around three steel plants using fabricated carbon traps for sampling and GC for analysis (Chattopadhyay, Chatterjee and Chakraborti 1996). The

authors attempted to estimate the risk of cancer based upon the observed levels and found it higher among the factory workers. In another study of BTX by the same group (Chattopadhyay *et al.* 1997), samples were collected in the same way as in the other studies at three locations in Calcutta. The study cited as likely principal sources automobile exhaust and emissions from coal-burning stoves which were estimated to number 5,280 per square kilometre in Calcutta. Benzene and other aromatic hydrocarbons including toluene, ethyl benzene and xylene were collected using Tedlar sample bags at six sites in Mumbai, reported at the Tenth National Symposium on Environment at Bangalore University (Srivastava *et al.* 2000). The samples were analysed by GC and toluene and benzene were found to be the dominant species. No decline in benzene levels was observed in Mumbai (Srivastava *et al.* 2000) compared to trends reported elsewhere.

Polycyclic Aromatic Hydrocarbons

In Mumbai, a group from the Indian Institute of Technology, Powai (Kulkarni and Venkataraman 2000) has reported studies on atmospheric concentrations of PAHs at two locations, Saki Naka and Powai, in Mumbai. They mentioned markers for various sources of PAHs in urban atmospheres. The sources included coal combustion, coke production, incineration, wood combustion, industries using fuel oil, gasoline-powered vehicles, and diesel-powered vehicles. The researchers noted that much similarity and overlap existed in profiles from different source categories. The qualitative source apportionment indicated that the motor vehicle emissions were the likely primary contributors with additional contributions from the use cooking fuels (animal manures, kerosene and liquefied petroleum gas, LPG) and industrial use of liquid fuels³. The authors suggested comprehensive measurements of inorganic and organic aerosol constituents in all seasons and of local source profiles to make quantitative source apportionment estimates. In another study (Venkataraman, Thomas and Kulkarni 1999) from the same institute, the size distributions of PAHs in Mumbai were analysed with the objective of studying the gas/particle partitioning in urban aerosols. An eight-stage Andersen impactor was used to collect the samples and PAHs were analysed using HPLC with ultra-violet (UV) absorption detection. Semi-volatile PAHs were predominant in coarse mode aerosols while non-volatile PAHs were predominant in fine mode aerosols. PAHs in ambient aerosols were also measured at five locations in Mumbai using HPLC with a UV detector (Sahu *et al.* 2001). The PAH composition of the aerosols depended on the nature of the site.

³ Pyrene (27%), benzo(a)pyrene (BaP-15%), and dibenzanthracene (12%) are quoted by the authors as the predominant PAH species in locally measured PAH profiles.

Qualitative source apportionment indicated that oil burning industries and vehicular emissions were likely primary contributors.

A study in Durg, industrial city in the state of Madhya Pradesh, reported PAH concentrations in the atmosphere (Pandey, Patel and Lenicek 1999). The ambient concentrations of PAHs averaged 4.66 nanograms per cubic metre (ng m^{-3}) on an annual basis. From good correlations among concentrations of lead, vanadium, benzo(a)pyrene (BaP) and benzo (ghi) perylene (BghiP), the authors suggested that motor vehicle emissions were major sources of PAHs.

Twelve species of PAHs in SPM were measured during winter (January and February) in Calcutta for 3 years from 1992 to 1994, both years inclusive (Chattopdhyay *et al.* 1998). Samples were collected at 5 busy road intersections within the city. The BSOM content of the air particulate samples collected was $10.1 \pm 1.9\%$. The lowest PAH concentration observed was 23 ng m^{-3} at Jadavpur (West Bengal) in 1993 and the highest was 191 ng m^{-3} at Maulali (West Bengal) in 1994. The global average concentration of PAHs from all samples was found to be $77 \pm 27 \text{ ng m}^{-3}$. The compositional patterns of the 12 PAH species monitored were very similar in all the samples. The average BaP concentration was $10.4 \pm 4.8 \text{ ng m}^{-3}$. BaP concentrations were found to be 61 times those of Melbourne and 69 times those of Hong Kong. The ratio of BaP to total PAHs for all samples was 0.12 ± 0.02 . There was evidence that stationary sources in the city of Calcutta that use coal as a fuel were the major emission sources of PAHs found in particles.

Summary

- Most studies seem to have been carried out using similar methods of collection and analysis. Sample sizes are not always given.
- In urban areas, automobile exhaust is cited as the primary source of VOCs together with the combustion of fossil fuels and wood.
- Almost all the studies recommend drawing up local source profiles to make quantitative source apportionment possible.

Recommendations

In order to estimate the emissions quantitatively in terms of sources, inventories will have to be drawn up. These must contain accurate information about the number and kinds of anthropogenic sources. Although biogenic sources of VOCs are not usually quantified as part of urban inventories, evaluation of vegetation commonly occurring in India must be carried out since data cannot be transferred from Europe or North America owing to differences in climate and vegetation.

Ammonia

The natural cycling of hydrogen is complicated and subject to the influence of human activities. Ammonia is one of the cycle's most variable components and—being the most abundant alkaline component of the atmosphere—is important in the neutralisation of acidic aerosols generated by the oxidation of SO₂ and NO_x. The oxidation of ammonia in soil may lead to the soil's acidification. Ammonia, after becoming neutralised, forms ammonium salts which are present in the aerosols of sub-micron size, cloud droplets and precipitation. Besides this, in regions with intensive livestock and agriculture associated with large emissions of ammonia, changes may occur in nutrient economy causing alterations in plant communities.

Several Indian studies report measurements of ammonia in different phases. One study also reports multi-phase simultaneous measurements at a site. A valuable inventory of emissions has been drawn up by Parashar, Kulshrestha and Sharma (1998) giving details based on preliminary estimates and not field measurements of anthropogenic versus natural emissions of nitrogen species. The paper concluded that ammonia levels were controlled by animals rather than fertilisers and that India's overall contribution to global emissions was less than one-tenth. A multi-phase simultaneous study, carried out at a suburban site in Agra, noted significantly that currently ammonia is present at sufficient levels in the atmosphere to neutralise sulphuric and nitric acids (S.P. Singh *et al.* 2001). In India, the basicity of coarse aerosols is a consequence of higher concentrations of sodium (Na), magnesium (Mg), and calcium (Ca) while the basicity of the fine mode is due to neutralisation by ammonia. Source apportionment was not an aim of the study.

A programme on NH₃ concentration measurements in Delhi was carried out for a five-year period from December 1982 to November 1987 (Kapoor, Singh and Tiwari 1992). The wind speed, temperature, relative humidity and rainfall were also measured to investigate their variation with NH₃ concentration. The study showed: (1) no specific variation of NH₃ concentration on a day-to-day basis; (2) maximum concentration was observed during a period of calm wind; (3) differences in NH₃ concentration between easterly and westerly winds were small although marginally higher for easterly winds; (4) a decrease in concentration was invariably found with increasing wind speed and temperature. The NH₃ concentrations, however, increased with increasing relative humidity. An attempt was made to explain these trends in terms of vertical ventilation. The dominant sources of ammonia appeared to be local.

The concentrations of NH₃ and nitric acid (HNO₃) at different sampling times and seasons were measured in Agra (Parmar *et al.* 2000a). The mean concentrations for the entire data set were $23.6 \pm 18.4 \mu\text{g m}^{-3}$ and $0.64 \pm 0.56 \mu\text{g m}^{-3}$, respectively. The average concentrations of NH₃ and HNO₃ in the monsoon season were 23.1 ± 5.1 and

$0.36 \pm 0.28 \mu\text{g m}^{-3}$ while in the winter mean values observed were $17.1 \pm 6.3 \mu\text{g m}^{-3}$ and $0.84 \pm 0.48 \mu\text{g m}^{-3}$, respectively. No statistically significant diurnal variation was observed for NH_3 and HNO_3 concentrations in both seasons. However, the levels of NH_3 were observed to remain nearly constant in winter at all the sampling times except for slightly lower levels in the early morning hours. HNO_3 concentrations were also lower in samples collected at dawn, but increased in the afternoon hours. Further, NH_3 and HNO_3 concentrations showed statistically significant seasonal dependence. Levels of nitric acid were higher in the winter ($0.84 \pm 0.48 \mu\text{g m}^{-3}$) and lower in the monsoon ($0.36 \pm 0.28 \mu\text{g m}^{-3}$). Higher concentration of HNO_3 in the winter would be a result of stable atmospheric conditions while scavenging by precipitation could lead to a decrease in concentration in the monsoon. The seasonal behaviour of ammonia is just the reverse of that observed for nitric acid with higher monsoon levels, consistent with the view that NH_3 originates largely from natural emissions which are at a minimum during the winter.

Sulphates

Several sources, both natural and anthropogenic, emit gaseous SO_2 into the atmosphere. Natural sources include dimethylsulphide (DMS) from the oceans and hydrogen sulphide (H_2S) from marshes and wetlands. Fluxes of biogenic sulphur from terrestrial vegetation and soils are much weaker than from aquatic ecosystems.

The major anthropogenic emitters of sulphur are fossil fuel combustion and smelters, mainly in the form of SO_2 . The contribution from biomass burning is thought to be relatively small.

The tropospheric sulphur cycle involves the oxidation of DMS and H_2S to SO_2 and then to sulphate followed by deposition as sulphates. The oxidation may occur by reacting with hydroxyls (OH^\cdot) and takes about a week in the gas phase. Oxidation can occur faster under cloudy conditions with SO_2 dissolving in cloud droplets, dissociating in the aqueous phase and reacting with aqueous-phase oxidants.

While extensive measurements of sulphate wet deposition fluxes are available, data on dry deposition are few. The dry deposition of SO_2 is also an important sink with the uptake of SO_2 at vegetation stomata being particularly efficient.

In India, several studies have reported sulphates in rainwater, dry deposition and aerosols (for example, see Khare *et al.* 1996; Reddy, Rama Rao and Murahari Rao 1999, Kulshrestha *et al.* 1995a).

A study conducted by Parmar *et al.* (1999) attempted to establish a relationship between SO_2 and corresponding sulphate (SO_4^{2-}), applying a correction factor for the soil content. SO_2 was measured using the West and Gaeke method and SO_4^{2-} by ion chromatography (IC). Several trace metals were also determined (iron, manganese,

chromium, zinc, nickel, cadmium and lead, or Fe, Mn, Cr, Zn, Ni, Cd and Pb). Their study showed that the oxidation of SO_2 to SO_4^{2-} was enhanced by dust particles with the metal ions playing a catalytic role.

Kulshrestha *et al.* (1998) reported the composition and association of size-differentiated aerosols in a suburban area in Agra. Fifty-eight percent of SO_4^{2-} was found in the fine size fraction (diameter $< 2 \mu\text{m}$) and 42% in the coarse size fraction. A SO_4^{2-} peak in the sub-micron range suggested secondary sulphate formation by the heterogeneous oxidation of SO_2 on alkaline particles of Ca and Mg but the total aerosol was alkaline by nature. Another study, by the same team, in Agra of dry deposition rates on polypropylene surfaces suggested that sulphates at the site were soil-derived or associated with the soil elements (Saxena *et al.* 1997). The study measured deposition velocities less than 1 centimetre per second (cm s^{-1}) for SO_4^{2-} and indicated that supermicron sulphur-containing particles may form an appreciable fraction of the total sulphur deposition. In a study carried out on bulk and wet deposition in Delhi, Kulshrestha *et al.* (1995a) found that the free acidity of rainwater was due to SO_4^{2-} rather than nitrate (NO_3^{-1}). The bulk samples were preserved using thymol and analysed by IC. Atmospheric aerosols were sampled at a coastal site (Vishakapatnam) by Reddy, Rama Rao and Murahari Rao (1999). Sampling was carried out using a high-volume sampler and estimated by turbidimetric methods. The authors ascribed the highest concentrations of pollutants to regional transport of pollutants rather than local sources.

On 6 June 1995, a fire engulfed a plastic scrap market in Delhi, affecting one-fourth of the city. Two studies (Jain, Kulshrestha and Parashar 1996, Jain *et al.* 1998) examined dry deposition fluxes of some species including SO_4^{2-} , and found that high deposition continued for almost 14 days after the incident. Sharma and Patil (1992a, 1992b) attempted source identification of aerosols in Bombay (now Mumbai), reporting SO_4^{2-} in TSP. Meteorological parameters were not presented, precluding the possibility of considering sources upwind of the sampling site.

Sulphate size distributions were measured at a coastal station in Mumbai in 1998 during the Indian ocean experiment (INDOEX) first field phase (FFP) (Venkataraman, Sinha and Bammi 2001). The paper examined meteorological, seasonal and source-contribution effects on sulphate aerosols and discussed potential effects of sulphate on the regional climate. The sulphate size distributions were largely trimodal with a condensation mode (mass median aerodynamic diameter, or MMAD, of $0.6 \mu\text{m}$), a droplet mode (MMAD of $1.9\text{--}2.4 \mu\text{m}$) and a coarse mode (MMAD of $5 \mu\text{m}$). Condensation mode sulphate mass-fractions were highest in concentration in winter, consistent with the high meteorological potential for gas-to-particle conversion along with low relative humidity. The droplet mode

concentrations and overall MMADs (in the droplet mode) were larger in the pre-monsoon and winter than in monsoon, implying sulphate predominance in larger sized particles within this mode. Coarse mode sulphate concentrations were lowest in the monsoon, when the continental contribution to sulphate was small and washout was efficient. In winter and pre-monsoon, coarse mode sulphate concentrations were somewhat higher, likely from SO₂ gas-to-particle conversion. Low daytime sulphate concentrations with a large coarse fraction, along with largely onshore winds, indicated marine aerosol predominance. High night time sulphate concentrations and a coincident large fine fraction indicated contributions from anthropogenic / industrial sources or from gas-to-particle conversion. Monthly mean sulphate concentrations increased with increasing SO₂ concentrations, relative humidity and easterly wind direction, indicating the importance of gas-to-particle conversion and industrial sources located to the east.



Characterisation of particulate matter

Understanding particulate air pollution is perhaps the most important aspect in developing an urban air quality management strategy in India and the rest of South Asia. This chapter describes some of the key studies conducted to date, focusing primarily on the chemical analysis of particulate matter and size distribution.

Metal analysis

Aerosols and dust in urban areas are known to be substantially enriched in several toxic trace elements compared to those from non-urban areas, exposing people in cities to higher levels of elements harmful to health.

Over the last decade, 15-20 studies have addressed the problem of pollution by heavy elements (including Cu [copper], Cr, Fe, Ni, Pb, Zn, V [vanadium], As [arsenic], Be [beryllium], Cd, Ti, Mn and Al [aluminium]). The water-soluble elements are reported more commonly, probably because of the ease of analysis.

The prevalent use of leaded gasoline in India has made the study of this element extremely important; indeed, most of the published work has reported Pb levels⁴. Lead was measured by Gaghate and Hasan (1999) using AAS and Wilson (1998) using colorimetric analysis. The former study reported highest lead concentrations in 1991 in Calcutta, followed by Delhi and Kanpur (Uttar Pradesh). The presence of lead was assumed to be due to automobile exhaust, and no further attempts made to apportion sources. Wilson (1998) studied seven traffic junctions in Bangalore and determined that lead was present in the atmosphere at concentrations far higher than the national ambient air quality standards for lead. In Lucknow city, N. Singh *et al.* (1997) evaluated lead in soil and vegetation along highways. Lead in rice, vegetables and milk from cows and buffaloes was measured using AAS. Bajwa and Ghosh (1999) measured lead, cadmium and zinc using AAS in Varanasi and Kanpur. The distribution and concentration of these elements in soil/plants was measured along roads with high and low traffic density. No attempt was made to apportion sources but tyre abrasion was cited as a source for cadmium and zinc. Regression analysis revealed that the dispersion of Pb, Cd and Zn in these habitats was dependent on the

⁴ Lead was phased out of gasoline in India in 2000.

intensity of vehicular traffic. The concentration of the metals, both in plants and soil, decreased with increasing distance from the road as well as increasing soil depth.

Another study measured lead concentrations in the atmosphere and children's blood in Mumbai to estimate the importance of lead emissions from gasoline-fuelled vehicles as a source of lead (Tripathi *et al.* 2001). They profiled exposure due to inhalation and ingestion as well as temporal variation and found that lead levels had decreased over the study period from 1984 to 1998. Ambient concentrations of lead were lower than the national air quality standards for lead but ingestion and inhalation were found to be important routes for children.

In Varanasi, one study analysed dustfall collected in jars of water exposed for one month (B.D. Tripathi, A. Tripathi and Misra 1991). The authors studied seasonal variations in concentration and analysed the water soluble and water-insoluble fraction, tarry substances, combustibles, ash, Ca and chlorine (Cl). A comparison was made of the levels of these species/substances between the sites selected and variations ascribed to the proximity of the site to possible sources such as coal depot and areas with high traffic density. Higher levels in the winter were ascribed to inversion at ground level. Tripathi, Ashawa and Khandekar (1993) reported the atmospheric deposition of Pb, Cd, Cu (copper) and Zn in Deonar, Mumbai. The sites at which these elements were measured were affected by emissions from industries such as petrochemicals, chemicals and paint manufacturing. The samples were collected in a tray whose bottom was constantly kept wet with 0.5% nitric acid to avoid possible re-suspension of deposited dust, and exposed for five to eight days. Analysis was carried out using differential pulse anodic stripping voltammetry. Tripathi (1994) measured lead using Gelman fibre glass filters in a high volume sampler in Varanasi. The filters were analysed for lead by atomic absorption spectrophotometry (AAS) and monthly variations were reported. The proximity of the sampling site to sources of lead such as vehicular traffic and refuse burning was cited as the explanation for observed ambient concentrations of lead.

In Nagpur city, Chutke, Ambulkar and Garg (1995) analysed for 30 elements in sixteen samples of pedestrian dust (dust on the ground) collected from industrial, commercial / residential sites, transport areas and near highways. Standard reference materials from the National Institute of Standards and Technology, USA were used for quality control and to validate the data. The method of analysis was instrumental neutron activation analysis (INAA). Elevated levels of arsenic, barium, bromine, copper, antimony and selenium were attributed to the nature of the site. However, no inventory or statistical analysis was carried out to apportion sources. The same group also analysed dust in ambient air in industrial, commercial and residential areas of four metropolitan cities (Delhi, Calcutta, Madras, and Cochin) and estimated the

levels of 27 elements by INAA. The concentrations were found to be highly variable for As, Ba, Br, Cu, Cr, Hg, Sb, Se and Zn and were explained on the basis of possible sources (Chutke *et al.* 1994). TSP concentrations were measured in Mt. Abu, Rajasthan by Negi *et al.* in 1996. This is not an urban area but correlation coefficients among elements in the dust showed mainly two components: wind-blown ground dust and particles arising from wood- and coal-burning. Factor analysis could not be carried out because the sample size was too small. Bhat and Pillai (1997) measured concentrations of Be in air, water and soil in the vicinity of a beryllium metal plant in New Bombay. Morin fluorescence and AAS were used for Be analysis. The Be levels in air, water and soil were found to be in the same range as elsewhere in the world.

Samanta *et al.* (1998) measured the concentrations of ten metals in SPM in Calcutta. Correlation coefficients and ratios with Fe were used to suggest sources. Chelani, Gajghate and Hasan (2001) measured RSPM and metal concentrations in Mumbai using a high volume sampler and glass fibre filter papers. Chromium, cadmium, iron, lead and nickel were measured using AAS and monthly averages of metal concentrations for each metal from three sampling stations were calculated for the period 1993-1998. The report did not aim at determining sources of the metals.

The size distribution of atmospheric aerosols was analysed in Dayalbagh, Agra during July to September 1998 (Parmar *et al.* 2000b). A 4-stage cascade particle sampler (CPS-105), which fractionated particles in sizes ranging between $0.7\ \mu\text{m}$ and $> 10.9\ \mu\text{m}$, was used. The filters were analysed for the major water-soluble ions. The average mass of aerosols was found to be $132\ \mu\text{g m}^{-3}$ and the aerosol composition was found to be influenced by terrigenous sources. The mass size distributions of the aerosols and the ions monitored— NH_4^{+1} , Cl^{-1} (chloride), NO_3^{-1} , K^{+} (potassium), Ca^{+2} , Mg^{+2} , SO_4^{-2} and Na^{+1} —were bimodal while that of F^{-1} was unimodal. SO_4^{-2} , F^{+1} (fluoride), K^{+1} and NH_4^{+1} dominated in the fine mode while Ca^{+2} , Mg^{+2} , Cl^{-1} and NO_3^{-1} were in abundance in the coarse fraction. Na^{+1} was found in both coarse as well as fine size fractions. Coarse mode SO_4^{-2} and NO_3^{-1} were ascribed to re-suspension of soil and formation by heterogeneous oxidation on soil-derived particles. Preponderance of K^{+1} in the fine mode is attributed to emissions from vegetation and from burning of plant materials. Ca^{+2} , Mg^{+2} , Cl^{-1} , and NO_3^{-1} were largely soil-derived and hence dominated in the coarse fraction. Equivalent ratios of $\text{NH}_4^{+1}/(\text{SO}_4^{-2} + \text{NO}_3^{+1})$ were calculated for both fine and coarse aerosols. The ratio for the coarse size fraction varied between 0.7 and 1.4 while that for the fine size fraction ranged between 1.4 and 1.9. These ratios show that the aerosols were basic for the most part, the basicity of the coarse mode was due to higher concentrations of soil-derived alkaline components while the basicity of the fine mode was due to acidity neutralisation by NH_3 .

Carbon analysis of RSPM

A small-scale study of carbon in RSPM was carried out by TERI in collaboration with the Max Planck Institute of Chemistry, Germany, in 2000-2001. Fifteen filters of RSPM samples collected in CAMPS by TERI at 3 stations were sent to the Max Planck Institute for carbon analysis. A thermal analysis method known as evolved gas analysis (EGA) was used for this purpose. Aliquots of filter samples were analysed for total carbon (TC) and black carbon (BC). Additionally filter punches were extracted in water in order to estimate how much carbonaceous material could be removed by the water, TC_{water} (this gives an idea of the water-soluble organic carbon, WSOC, content of the sample). The results are shown in Table 4.1.

Table 4.1 Carbon analysis in RSPM

Date	Location	Height (m)	RSPM ($\mu\text{g}/\text{m}^3$)	TC ($\mu\text{g}/\text{m}^3$)	TC/RSPM (%)	BC ($\mu\text{g}/\text{m}^3$)
13.08.00	GNP	4	193	42	22	17
23.10.00	GNP	4	503	177	35	88
28.12.00	GNP	4	702	240	34	115
28.12.00	GNPR ^a	14	542	341	63	216
15.01.01	GNP	4	385	134	36	55
15.02.01	ITO	10	581	115	20	47
13.08.00	ITO	10	108	48	45	—
23.10.00	ITO	10	292	165	56	84
15.01.01	ITO	10	333	128	39	76
15.02.01	JNU	8	150	60	40	28
13.08.00	JNU	8	72	28	38	17
23.10.00	JNU	8	282	61	22	—
15.01.01	JNU	8	410	161	39	91
15.01.01	JNU	8	336	88	26	—
15.02.01	JNU	8	166	41	25	28

^a GNP and GNPR are at same location but at different heights.

Notes: GNP Gurunanak Public School; JNU Jawaharlal Nehru University. — not available.

The table shows that

- TC and BC mass concentrations were high, as much as 341 and 216 $\mu\text{g m}^{-3}$, respectively.
- Water-soluble organic carbon constituted about 40% of the total carbon content.
- The ratios of $BC_{\text{water}}/\text{TC}$ (from regression analysis = 0.44) and BC/TC (from regressions analysis = 0.61) were high, suggesting predominant contribution of fossil fuel over biomass. The combustion of biomass typically gives BC/TC ratios in the neighbourhood of 0.1.

During the Indian Ocean experiment-intensive field phase (INDOEX-IFP), measurements were carried out in Mumbai in January-March 1999 to study the size and chemical characteristics of surface aerosol. PM₁₀ samples were collected at the height of 10 m at the Indian Institute of Technology, Mumbai. This site, about 10 km inland from the coast, represents a background urban site. A summary of the results of this study is presented in Table 4.2.

Table 4.2 Average concentration of PM₁₀ and chemical constituents measured in Mumbai during INDOEX-IFP

Species	Period 1 (Jan '99 – early Feb '99)		Period 2 (Mid Feb '99 – end March '99)	
	Concentration ($\mu\text{g m}^{-3}$)	Contribution (%)	Concentration ($\mu\text{g m}^{-3}$)	Contribution (%)
PM ₁₀	182±48 ^a		128±27 ^a	
OC/BC	3.1±0.5		2.0±0.3	
Total carbon / PM ₁₀	52.2±16.3	28.4±2.6	39.1±13.0	30.0±4.0
Total ions / PM ₁₀	32.6±3.7	18.6±3.5	34.1±21.8	21.9±8.8
Total elements / PM ₁₀	6.16±0.43	3.6±0.4	4.70±0.39	3.6±0.2
Unexplained	90.60±7.87	49.7±12.6	50.18±10.05	39.0±14.5

^a mean ± 1 standard deviation of 3 samples in period 1 and of 4 samples in period 2

Source. Venkataraman *et al.* 2001

The result indicate the aerosol contains 30% carbonaceous and 20% ionic constituents, with the unexplained balance likely to contain NH₄⁺ ion, which could not be measured in this study. Low OC/BC ratios reveal the relative predominance of carbonaceous aerosols and high non-sea-salt sulphate contributions pointed to anthropogenic origins of the sulphate. High potassium and black carbon concentrations measured in the samples collected during January to early February were likely from a local biomass burning source. Crustal sources dominated the aerosol during late February-March, especially in the afternoon periods (Venkataraman *et al.* 2001).

It is informative to compare the above results with those from another study (Mayol-Bacero *et al.* 2001), not confined to India but conducted over the Indian Ocean region in February and March 1999 at altitudes ranging from 0 to 6.5 km. The INDOEX programme analysed for TC, BC and OC in PM_{1.3} (particles smaller than 1.3 μm). The ratios of BC to TC (0.42±0.09) and OC to BC (0.77±0.27) observed suggested that between 60% and 80% of the aerosol originated from fossil fuel and between 20% and 40% from biomass combustion. Emission inventories would point to the combustion of biomass contributing much more to the total aerosol mass in the Indian subcontinent, and the authors were not able to explain this seeming discrepancy.

The Indian-subcontinent Megacities Aerosol Campaign, an Indo-U.S. project, is currently underway to determine the annual and seasonal PM_{2.5} mass and chemical composition in Delhi, Mumbai, Calcutta and Chandigarh. Teflon, quartz and nylon filters are used and analysed for BC, EC, NH₄⁺, SO₄²⁻, Cl⁻ and NO₃⁻. The findings of this campaign should increase the knowledge base on particles.

Summary of elemental and carbon analyses

- Most of the published reports have focused on heavy elements.
- The methods of sample collection have not always been the most appropriate (particularly dustfall). AAS has been most commonly used for analysis.
- The levels of elements have been found to be correlated with the characteristics of the site, such as the type of anthropogenic activities taking place in its vicinity. Soil has been cited as a significant contributor in several studies.
- A study which analysed for total and black carbon in PM₁₀ collected in Delhi in 2000-2001 found that total carbon accounted for about one-third of PM₁₀, which is similar to the results reported in other countries. The ratio of black carbon to total carbon was comparable to those found in the INDOEX executed in February and March of 1999 over the Indian Ocean region. These results suggest significant contributions from the combustion of fossil fuels rather than biomass (such as wood and leaf burning).

Dry deposition studies

Although it is probable that dry deposition is by far the most dominant deposition process in India, relatively little research has been conducted using surrogate surfaces. These include wet/dry open buckets, petridishes, filter paper, Teflon plates, and coated and uncoated glass (Saxena *et al.* 1992). No studies have been reported on model approaches to dry deposition.

Kulshrestha *et al.* (1995a) collected samples of dry deposition in Delhi at two heights, 30 m and 13 m, to understand the influence of soil-derived particles. Source apportionment was not the primary aim of the paper. There have been attempts to determine sources in almost all the Indian studies (Khare *et al.* 1996, Chutke, Ambulkar and Garg 1995, Negi *et al.* 1996, Pandey, Patel and Subrt 1998, Reddy, Rama Rao and Murahari Rao 1999, Samanta *et al.* 1998, Satsangi *et al.* 1999, B.D. Tripathi, A. Tripathi and Misra 1991). The methods used have included simple correlation analyses and relations with meteorological variables and prominent sources (Pandey, Patel and Subrt 1998, Negi *et al.* 1996, Satsangi *et al.* 1999, Saxena *et al.* 1994). Enrichment factors have also been calculated by a few researchers to determine broadly whether the species measured were crustal (soil-based) or non-

crustal and of anthropogenic origin (Khare *et al.* 1996, Pandey, Patel and Subrt 1998).

Size distribution of particles

Apart from the NEERI monitoring and the recently launched programme by CPCB to routinely measure PM₁₀ in a small number of cities, there have been few other projects that have seriously measured particles of different sizes.

A study during the monsoon season of 1990 in the highly industrialised zone, Chembur-Trombay, of Mumbai measured the mass size distribution of aerosols using a multi-stage Andersen Sampler (Khemani *et al.* 1994). Measurements were carried out for a period of seven days near a fertilizer factory-refinery complex. Two 6-hour samples of aerosols were collected every day in the morning (07:00-13:00) and in the evening (15:00-21:00). One sample was taken continuously during the seven days. TSP was also measured during the same period. The results indicated that coarse particles ($>2.1\ \mu\text{m}$) accounted for 54.6% of TSP and fine particles ($<2.1\ \mu\text{m}$) accounted for 45.4% during the rainy season. The aerosols showed a bimodal distribution, one peak in the fine size range ($0.65\ \mu\text{m}$) and another peak in the coarse size range ($4.7\ \mu\text{m}$).

In situ measurements of mass concentration of size-distributed aerosols were carried out using a 10-stage quartz crystal microbalance cascade impactor (QCM-CI), which gives real time output data, with an upper cut of $25\ \mu\text{m}$ in an industrial belt in an eastern suburban region of Mumbai (Sharma and Patil 1992a and 1992b). Samples were taken at two locations from January 1989 to March 1990 at a frequency of one (24-hour) sample every six days at each site. Aerosol samples were also collected by the conventional high volume sampler for comparison and analysed for size distribution using a centrifugal analyser system and an image analyser system. TSP samples were also collected during the same period. The ambient concentrations of particles collected using the high-volume sampler were much higher than those collected by QCM-CI at both sites (180 and $541\ \mu\text{g m}^{-3}$ at the two sites by high volume sampling compared to 86 and $110\ \mu\text{g m}^{-3}$ by QCM-CI, respectively). The higher concentrations given by the high volume sampler were as expected since the sampler collected particles with diameters well above $40\ \mu\text{m}$. The concentrations of particles smaller than $25\ \mu\text{m}$ as well as their size distributions were approximately the same between the two instruments. One important conclusion of the study was that the percentage of PM_{12.5} in PM₂₅ was as high as 85%–90%, irrespective of sample collection and measurement techniques in the study. The percentage of PM_{3.2} in PM₂₅ was found to be 58%–63%.

Sharma and Patil (1991) reported the results on spatial and temporal variation of atmospheric particulate concentration using a QCM-IP. The study was carried out at two locations in the Bhandup-Thane belt, an industrial belt in an eastern suburban region of Mumbai. The sampling period covered the winter season, said to be the worst period for pollution, from October 1989 to March 1990. Particles were segregated into 10 size fractions with aerodynamic diameters ranging from 25 μm to 0.05 μm . The average concentrations of particles smaller than 12.5 μm and 6.4 μm — $\text{PM}_{12.5}$ and $\text{PM}_{6.4}$ —were found to exceed the standards set by US EPA for PM_{10} . Authors attempted to develop an empirical regression model to correlate hourly observations of particulate concentrations and wind velocity. Diurnal measurements showed that concentrations of size-fractionated particles were higher at night than during the day for the most part. The concentrations of aerosols smaller than 3.2 μm increased with distance from the ground and reached a maximum around 9 m, and then decreased above this height. In general, more than 85% of aerosols (all of which were smaller than 25 μm in diameter) were smaller than 12.5 μm .

Kumar (1998) carried out a study in Mumbai using a ACM-IP at two traffic junctions in the period July-September 1991. The samples were collected on an hourly basis during the day, mostly on wet days. Since the soil surface was wet, re-suspension and re-entrainment of soil should have been minimal, and the data would be expected to represent the particle size distribution related to vehicular emissions. The results showed that more than 96% of the PM_{25} aerosols were less than 12.5 μm .

Size-fractionated aerosol samples were collected at a suburb of Agra during December 1992- March 1993 at a height of 8 m above ground using an eight-stage Andersen cascade impactor (Kulshrestha *et al.* 1995c, 1998). Five samples were collected in each study. The upper size cut was 30 μm . The results indicated a bi-modal distribution and 52% of the particles were smaller than 2 μm in diameter.

Using an eight-stage Andersen sampler, a group in Delhi studied the size distribution in winter (between October 1998 and December 1998) at a height of 12 m above ground level (Gadi *et al.* 2000). Samples were collected for 3-4 days at a time, averaging 72 hours in duration. Fine particles (<2 μm) contributed 68% to the total mass of PM_{10} .

Size-fractionated aerosol samples were collected from two ambient monitoring sites in Mumbai during the winter of 1996-1997 using an eight-stage Andersen sampler (Venkatraman, Thomas and Kulkarni 1999). The impactor had 50% cut-off aerodynamic diameters of 10, 9, 5.8, 4.7, 3.3, 2.1, 1.1, and 0.65 μm . Samples were collected over 72 hours. The particle size distributions were bimodal with a fine mode mass median diameter of 0.38-0.45 μm , and a coarse mode mass median diameter of 2.7-4.7 μm . About 55% of particle mass was in the sub-micron range.

Nautiyal (2000) carried out a study in Mandi-Gobindgarh, an industrial town, and in Morinda, a non-industrial town, in Punjab using a two-stage fractionator ($PM_{2.5}$ and PM_{10} , sequential filter unit). Fifty samples were collected from August 1999 to May 2000 in both areas. The sampling time was either 12 or 36 hours. The sampling height was varied between 6 m and 12 m. The levels of $PM_{2.5}$ varied from $24 \mu g m^{-3}$ to $90 \mu g m^{-3}$ in Morinda and $32 \mu g m^{-3}$ to $100 \mu g m^{-3}$ in Gobindgarh. The $PM_{2.5}/PM_{10}$ ratio was found to be 0.42 at both sites.

Summary

- Very few studies have examined the size distribution of particles. These studies have been mostly of short duration, small sample size, and have not adequately documented seasonal variation.
- There are indications from the NAMP data that PM_{10} make up one-third to two-thirds of TSP.
- $PM_{2.5}$ has been found to constitute about one-half of PM_{10} .
- One recent study which analysed for total and black carbon in PM_{10} found that total carbon accounted for about one-third of PM_{10} , which is similar to the results reported in other countries. The ratio of black carbon to total carbon was comparable to those found in INDOEX in February and March of 1999 at altitudes ranging from 0 to 6.5 kilometres over the Indian Ocean region. These results suggest significant contributions from the combustion of fossil fuels rather than biomass (such as wood and leaf burning).
- There is essentially no information on background particulate concentrations or the characteristics of particulate matter in background areas.



Source apportionment of particulate matter

Description of studies

No more than a dozen source apportionment studies appear to have been conducted in India. Most were carried out in the period 1989-92. These studies are summarised in Table 5.1.

Most studies have concentrated on TSP. However, analysis of TSP is not as helpful as analysis of smaller particles for two reasons. First, from the point of view of health impact, large particles are not nearly as damaging as smaller particles which can penetrate deep into the respiratory tract, especially into the alveolar regions of the lung. Animal studies indicate a potentially important role of ultrafine particles less than $0.05\text{ }\mu\text{m}$ in diameter. These particles are cleared only very slowly from the lung, and they can penetrate the pulmonary interstitium, inducing inflammatory responses. For this reason, regulators in an increasing number of countries are concentrating on enforcing health-based air quality standards for PM_{10} , and have recently begun to introduce standards for $\text{PM}_{2.5}$. A relevant policy question is therefore what is contributing to ambient concentrations of $\text{PM}_{2.5}$ or particles in some other small size fraction.

Second, many anthropogenic sources of particulate air pollution emit small particles—vehicular particulate emissions, for example, fall predominantly in the sub-micron range—while natural sources (such as wind-blown dust) contribute significantly to large-size particles. Analysis of TSP would thus tend to highlight the importance of dust and other natural sources of particles at the expense of anthropogenic sources, when these particles from natural sources may not be all that important from the point of view of public health policy. The Airborne Particles Expert Group (1999) in the United Kingdom reported that road traffic sources were responsible for only 25% of PM_{10} but as much as 60% percent of $\text{PM}_{0.1}$ (particles smaller than $0.1\text{ }\mu\text{m}$), considered much more damaging to public health than PM_{10} .

The findings described in this chapter should therefore be interpreted in light of the above codicils. Most studies examining TSP would be expected to show that natural sources are dominant contributors to particulate air pollution. Moreover, as will be shown, none of the studies have included carbon analysis, thereby precluding the possibility of investigating the combustion of fossil fuels and biomass in depth. The preponderance of TSP studies and the absence of carbon analysis are two serious

Table 5.1 Summary of source apportionment studies in India

City	Type of site	Year	Duration of study	Number of samples	Elements	Analytical method	Apportionment method	Sources identified	Reference
Chandigarh	- Residential	1994-96	6 months	95 at each site	S, Cl, K, Ca, Ti, V, Cr,	EDXRF	Factor analysis	- Soil dust	Bandhu <i>et al.</i> 2000, Bandhu <i>et al.</i> 1998
	- Suburban/- industrial - City				Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Pb			- Refuse burning - Field burning - Vehicles - Smelters	
Mumbai	centre/commercial	1993-94	1 year	104	Al, Br, Ca, Ce, Cl, Co, Cr, Fe, Hg, K, La, Na, Pb, S, Sb, Sc, Si, Sm, Ti, Zn	EDXRF	Factor analysis	- Re-suspended soil - Vehicles - Sea salt - Refuse burning	Meenakshy, Negi and Sadasivan 1996
	Industrial								
Mumbai	2 Traffic junctions/ industrial	1991-92	1 year	52 at each site	Al, As, Ca, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb	AAS	Factor analysis-multiple regression	- Road dust (crustal / re-suspension) - Vehicles - Marine - Metal industries - Coal combustion	Kumar and Patil 2001
Agra	Industrial	1991-92	1 year	104?	Cu, Fe, Mn, Zn, Ni, Cd, Mg, Pb, Al, Na, K, Ca, Si, Ca, Cr	AAS IC	PCA	- Soil - Road dust - Foundries - Copper wire unit and diesel engines testing - Cr and Ni plating	Khare, <i>et al.</i> 1996

City	Type of site	Year	Duration of study	Number of samples	Elements	Analytical method	Apportionment method	Sources identified	Reference
Vehicles									
Agra	Commercial	1991-92	1 year	40	Cu, Fe, Mn, Zn, Ni, Cd, Mg, Pb, Al, Na, K, Ca, Si, Ca, Cr	AAS IC	PCA	- Soil - Industrial sources - Wood combustion - Brick kilns	Kulshrestha et al. 1995b
Mumbai	Industrial	1989	1 year	60	19 elements	ICP-ES UV XRF	Chemical mass balance	- Crustal - Marine - Vehicles - Combustion - Ferrous industries - Non-ferrous industries	Sharma and Patil 1994
Mumbai	Industrial	1989-90	15 months	96	Based on PM size classes	QCM-CI	Factor Analysis	- Age dominated aerosols - Gas-to-particle conversion (vehicle exhaust) - Soils - Marine sources	Sharma and Patil 1992a
Mumbai	Industrial	1989	1 year	60	Al, Ca, S, Fe, Sb, K, Ti, Cl, Na, Cu, Pb, Br, Zn, Ni, Cr, V, Mn, Si, As	ICP-AES EDXRF	Factor Analysis	- Soil - Marine - Oil burning - Coal - Ferrous industry - Vehicles - Secondary sulphate	Sharma and Patil 1992b
Mumbai	Industrial	1985	10 weeks	?	28 elements	EDXRF	Factor analysis	- Crustal	Sadasivan and

City	Type of site	Year	Duration of study	Number of samples	Elements	Analytical method	Apportionment method	Sources identified	Reference
						INAA		<ul style="list-style-type: none"> - Refuse incineration - Coal and firewood - Oil refinery - Sea salts - Fertilizer factory 	Negi 1990
Bangalore	Residential	1980-81	1 year	?	Al, Si, S, Cl,	EDXRF	Factor analysis	Nagpur	Negi,
Mumbai	Industrial				K, Ca, Ti, V,			- Soil dust & fly ash	Sadasivan and
Nagpur	Commercial				Mn, FE, Ni,			- Refuse combustion	Mishra 1987,
Jaipur	Industrial				Cu, Zn, Br, Rb, Sr, Pb			- Clay minerals	Negi,
								- Mining	Sadasivan and
								Mumbai	Mishra 1988
								- Soil dust	
								- Refuse combustion	
								- Sea salt	
								- Oil refinery	
								- Fuel oil	
								Jaipur	
								- Soil	
								- Refuse combustion	
								- Rock salt	
								- Copper mine	
								Bangalore	
								- Soil	
								- Non ferrous industries	
								- Battery factory	
								- Heavy minerals	

City	Type of site	Year	Duration of study	Number of samples	Elements	Analytical method	Apportionment method	Sources identified	Reference
Hyderabad Kanpur Mangalore Mumbai	Industrial Commercial Residential		1 year	60-80 / location	Al, Fe, Ni, Cu, Cr, Cd, V, Zn, Mn, Pb, Hg, Br, Cl	AAS	Factor analysis	- Soil dust - Coal/refuse burning - Vehicles - Industries - Sea salt	Sengar 1989
Nainital	Rural (background)	1982-83	6 months	?	18 elements	?	Factor analysis	- Biomass combustion - Natural sources	Mahadevan, Negi and Meenakshy 1989

Notes All studies based on TSP samples, except Meenakshy, Negi and Sadasivan (1996), which is based on PM₁₀ and Sharma and Patil (1992a), which is based on size fractionated aerosols. Mangalore is in Kanartaka, Nainital in Uttaranchal in northern India.
ICP-ES: Inductively coupled plasma-emission spectrophotometry

limitations of the studies carried out in India to date.

Among the recent studies, Bandhu and co-workers identified five prominent sources in Chandigarh: soil dust, refuse burning, field burning (agricultural residues), vehicles and smelters (Bandhu *et al.* 2000; Bandhu *et al.* 1998). Bandhu *et al.* (2000) measured sixteen elements in aerosol samples from industrial, commercial and relatively clean zones in the city. Energy dispersive EX-ray fluorescence (DXRF) and photon-induced X-ray emission (PIXE) were used for the analyses and PCA applied to identify the major sources. Possible sources included soil dust, and such anthropogenic sources as refuse-burning, motor vehicle exhaust and industrial activities (iron foundry and lead recycling). The ratio of bromine (which is added to gasoline as ethylene dibromide when tetra alkyl lead is used as a gasoline octane booster) and lead concentrations (Br/Pb) suggested that vehicular traffic was not the main contributor of lead in this study.

A study in Mumbai focused on source apportionment at two traffic junctions (Kumar and Patil 2001). A factor analysis-multiple regression technique was used for quantitative apportionment of the sources contributing to SPM. Five possible sources were identified: road dust, vehicular emissions, marine aerosols, metal industries, and coal combustion. A quantitative estimation, the only one available in the open literature, indicated that road dust contributed to 41%, vehicular emissions to 15%, marine aerosols to 15%, metal industries to 6%, and coal combustion to 6% of the SPM at one of the traffic junctions (Saki Naka). The corresponding figures for the other junction (Gandhi Nagar) were 33%, 18%, 15%, 8%, and 11%, respectively. Due to limitations in source marker elements analysed, about 16% of the remaining SPM at these two junctions could not be apportioned. Of the observed lead in the SPM, the analysis apportioned 62% to vehicular emissions, 17% to road dust, 11% to metal industries, 7% to coal combustion, and 3% to marine aerosols. Thus, even at high traffic density junctions it was observed that levels of SPM and lead were not contributed solely by vehicle tail-pipe emissions.

Pandey, Patel and Subrt (1998) used a high volume sampler to collect particulate trace elements in the city of Bhilai in Chattisgarh in central India at an urban industrial location. Inductively coupled plasma (ICP) was used for elemental analysis while anions were determined by IC. High enrichment ratios of the elements with respect to their values in the earth's crust, and correlations among Zn, Pb, Cu, Cd, As, Be and Cl suggested contributions by non-ferrous metallurgical operations, diesel exhaust and residual oil combustion. Copper and zinc were attributed to smelting operations and coal combustion. Iron, manganese and titanium were thought to be from crustal sources, ferrous metallurgical operations and power plants.

Only one study has investigated source apportionment of PM₁₀ aerosols (Meenakshy, Negi and Sadasivan 1996). About twenty elements were measured over a year in Chembur, Mumbai. Factor analysis carried out showed four pollution sources: re-suspended soil dust, burning of refuse and vegetation, sea-salt and auto emissions. The soil-derived dust was found to be the major source for larger size particles whereas refuse burning and auto-exhaust were the major sources for smaller size particles.

Particulate matter was collected from an industrial site in Agra and analysed for the ionic species Na, K, Ca, Mg, Fe, Cu, Mn, Zn, Cd, Pb, Al, Cr, Ca_t (total calcium, soluble and insoluble), F, Cl, NO₃⁻¹, SO₄⁻² and NH₄⁺¹, and SiO₂, SO₂ and NO_x (Khare *et al.* 1996). Correlation matrix and enrichment factor analysis revealed that both crustal and non-crustal sources contributed to the aerosols. Principal component analysis resolved the following sources as contributing to particulate matter: soil, road dust, emissions from foundries, testing of diesel engines during engine manufacture, electroplating and automobile exhaust. It is not clear from this study how the authors distinguished road dust from either soil or automobiles. During the same period another study was also conducted in Agra, this time near the Taj Mahal, where the area can be characterised as a commercial / residential area (Kulshreshta *et al.* 1995b). Geometric mean enrichment factors of elements indicated two groups: one having enrichment factors less than 7 comprising Na, K, Ca, Mg, Fe, Al, Mn, and Si (crustal), and the other having enrichment factors greater than 13 comprising Ni, Cu, Zn, Pb, and Cd (non-crustal). Principal component analysis revealed the association of the first principal component with soil-derived elements while the second, third, and fourth principal components were associated with industrial processes, wood combustion and brick kilns, respectively. The wood combustion was associated with Na, K, and Ca. Brick kilns as a source were identified because of the high loadings for Si and SO₂, implying the use of sand and coal. Strangely, vehicles were not identified as a source at this site, despite the heavy traffic that the Taj attracts.

Sharma and Patil (1991) collected aerosol samples in an industrialised region of Mumbai and analysed 27 chemical species using ICP-emission spectroscopy (ES), EDXRF, and UV-VIS (UV-visible) spectrophotometry. Whatman 41 filter papers were used to collect samples with a high volume sampler. Although the number of samples analysed is not mentioned, a seven-factor model represented seven major sources at the two sites studied. Soil-related elements were attached with more than one factor indicating a collinearity of sources. Sources such as ferrous and non-ferrous industrial emissions and combustion processes—refuse-, oil- and coal-burning, road transport and secondary emission sources—were reported as contributors.

The only TSP source apportionment study based on chemical mass balance was carried out at three sites in an industrial area in Mumbai based on 19 elements (Sharma and Patil 1994). The US EPA chemical mass balance model was used. Seven major types of sources were identified and the performance of the model was evaluated at different sampling locations. Model results were unsatisfactory at highly polluted sites in the study area. The US EPA source profiles were found to be unsuitable for Indian conditions, pointing to the need for site-specific source profiles in future studies. Another study conducted by the same authors during the same period in Mumbai is unique in that instead of performing factor analysis on elements, they chose to do the analysis on particle size distribution data (Sharma and Patil 1992a). They concluded that aerosols of size 0.05-25 μm in diameter can be divided into four size groups. The four factors may be considered to represent four source types depending upon the size of particles emitted from them. The study could identify vehicles, wind-blown soil and marine aerosols as sources. Other studies in Mumbai have been able to identify combustion sources but have not differentiated further into different fuel use such as industrial versus motor vehicular (Sadasivan and Negi 1990; Negi, Sadasivan and Mishra 1988).

A study in four cities (Sengar 1989) on TSP concluded that the first factor represented crustal soil as the highest contributor in all the cities. This source contributed approximately half of the total variance in the system, suggesting that soil was the major source of Indian urban dust. The second dominant source was found to be coal/refuse burning. Motor vehicle source was also common but its strength varied from place to place.

A study conducted in a remote rural area could identify biomass combustion and natural sources as contributors to particle mass, thus demonstrating the ability of factor analysis to provide logical explanations in most situations (Mahadevan, Negi and Meenakshy 1989).

Data quality and interpretation issues

Some of the data quality and interpretation issues specific to source apportionment are discussed below.

- In some studies the sample size does not seem to be sufficiently large.
- Carbon has not been analysed, seriously limiting the scope of the studies.
- It is difficult to compare the results across studies because the set of elements chosen do not completely overlap.
- Some studies have also included total mass concentrations in the factor analysis model, while others have not.

Summary

- All studies but two to date have looked at TSP. Only one study has examined PM₁₀, and another size-fractionated particles. Only one study, on TSP, has explicitly quantified source contributions.
- None of the studies have analysed particles for carbon, seriously limiting the ability to examine combustion of fossil fuels and biomass in detail.
- Barring a few studies, most workers have used correlation analysis to suggest sources. Only a few have used the more reliable PCA coupled with enrichment factor analysis.
- Most studies have confirmed that natural dust is the predominant source of TSP.
- The one study examining PM₁₀ found natural dust to be the predominant source.
- Only one study has explicitly quantified the source contributions. At two traffic junctions road dust contributed 33%–41%, vehicular emissions 15%–18%, marine aerosols 15%, metal industries 6%–8%, and coal combustion 6%–11% of TSP.
- Vehicular sources have typically been lumped together with all other fossil fuel combustion sources.
- Wood and refuse burning is also identified as important sources.
- Even within urban areas most studies have chosen industrial locations. Typical downtown or residential areas have so far not been examined
- Seasonal variations in source contributions have not yet been studied.
- A couple of studies have identified small stationary sources of combustion as being important.
- Agricultural sources have not been considered in any study.

6 Emission inventories and air quality modelling

Emissions inventory

Comprehensive emissions inventories are limited to mega cities such as Mumbai and Delhi. Even these are sketchy because the data needed to construct emission inventories such as fuel use and suitable emission factors are not available for many sources. Instead, emission factors are simply adopted or extrapolated from other studies conducted in high-income countries. The data on the type of industries, fuel use patterns, and pollution control devices that are required to estimate the emissions are not easily available.

Emission factors

The emission factors vary widely depending on the type of technology used, fuel type and quality, age of the equipment, maintenance, type of equipment or the vehicle, the condition of the road, and so on. CPCB sponsored IIT, Khargpur (West Bengal), to undertake a project for developing emission factors for thermal power plants. Based on the study conducted by the IIT and various reports of NPC and NEERI, CPCB proposed the following emission factors (Table 6.1).

Table 6.1 Emission factors for thermal power plants

Fuel	Pollutants	Emission factor (kilograms/tonne)
Coal	SPM (controlled emission)	1.2
	SO ₂	16.60S*
	NO _x	2.64
Lignite	SPM (controlled emission)	0.64
	SO ₂	13.50S*
	NO _x	7.40
Gas	NO _x	2800 kg/10 ³ Nm ³ of gas

S* = weight percent sulphur in coal; Nm³ normal cubic metres

Source: Minutes of the 13th meeting of Peer & Core Expert Committee organised by CPCB on Development of Emission Factors for Thermal Power Plants on 31st May 1996

SPM emissions depend on the ash content of the coal and efficiency of the control systems (such as electrostatic precipitators, ESPs, and bag filters) installed. During discussion with experts, it was pointed out that the SPM emission factors were on the conservative side. The domestic coal, which is what is largely used in Indian power

plants, is high in ash content (about 30%–50%) but low in sulphur (less than 0.5%). In addition, the silica and alumina content in the ash is also high. This results in high resistance for the fly ash and makes it difficult for conventional ESPs to collect fly ash efficiently. The efficiency of the existing ESPs ranges from 85% to 95% (Kandlikar and Ramachandran 2000). In contrast, the efficiency of pollution control devices was assumed to be greater than 99.5% in the above emission factors. This raises a doubt about the suitability of the emission factors. During the review of these emission factors, representatives from power companies stated that the measured NO_x values were higher and recommended that NO_x emission factors be reconsidered in the light of the measured values.

Large variations in the emission factors for vehicles are also expected, and the vehicles in India and the rest of South Asia are no exception. More specifically, vehicular emission factors depend on vehicle technology, vehicle age, mechanical state of the vehicle (how well it has been serviced and maintained, amongst others), vehicle driving cycle, ambient temperature, and fuel and lubricant quality. In South Asia, vehicle maintenance tends to be poor, and roads are often heavily congested, resulting in low vehicle speed. In addition, fuel adulteration is common. Emission factors that take into account these conditions are not available. As a result, the emission factors used in studies contain large error margins. The compilation of emission factors used in various studies for vehicular emission estimation in India is given in Table 6.2. The table shows that large differences in the emission factors exist.

Table 6.2 Compilation of emission factors used in various studies for vehicular emission estimation in India, grams per kilometre

Emission factors for vehicle category	CPCB 1989	Kandlikar and Ramachandran 2000	Bose 1998	Shah and Nagpal 1997
Gasoline cars				
CO	40	25(40)	9.5	
HC	6	5 (40)	1.5	
SO ₂	0.08	-	0.15 ^a	
NO _x	3.2	3 (6)	1.9	2.7
SPM	0.33	-	-	0.2
PM ₁₀	-	0.4 (0.5)	0.25	0.2
Diesel cars				
CO	1.1	2 (4)	1.1	-
HC	0.28	1 (2)	0.28	-
SO ₂	0.39	-	0.93 ^b	-
NO _x	0.99	1.1 (1.4)	1.4	1.4
SPM	0.45	-	0.6	0.6
PM ₁₀	-	1.5 (2.0)	-	0.6
2-wheelers				
CO	17	15 (20)	8.3	-
HC	10	10 (25)	5.18	-
SO ₂	0.07	-	0.05 ^a	-
NO _x	0.02	0.3 (0.5)	0.10	-
SPM	0.2	-	0.5	-
PM ₁₀	-	0.4 (0.6)	-	-
Buses and trucks				
CO	12.7	3 (5)	12.7	-
HC	2.1	2 (4)	2.1	-
SO ₂	1.5	-	2.5 ^b	-
NO _x	21	10 (15)	21	-
SPM	0.75	-	2	0.68
PM ₁₀	-	1.5 (3)	-	0.68

^a The sulphur content in gasoline is 0.15% (W/W); ^b the sulphur content in diesel is 0.5% (W/W)

Note In the Bose study the emission factors for gasoline cars are for post-1984 model without catalytic converters; values given in parentheses are the upper end of the emission factor

Fuel use data

To estimate emissions from the transport sector, fuel consumption can in principle be calculated from two different methods. One is to take the number and type of vehicles, and calculate fuel usage based on assumptions about fuel economy and annual distance travelled. Another is to use fuel sale figures which are normally available in petroleum statistics. Both methods have limitations. The transport statistics give information on the number of vehicles registered. The information on

number of vehicles on the road is limited because vehicle scrappage is often not recorded. Information on fuel economy is not readily available, especially since fuel economy depends on a number of factors, including the driving cycle, the mechanical state of the vehicle, and the type of fuel used. Detailed data on the age distribution of vehicles are not available, nor are data on annual distance travelled. The supply side data give the total sales figures for diesel and gasoline. Although their major consumption is in the transport sector, a sizable fraction of diesel is used in small generators and other non-transport activities, but the data on these activities are again not available. Given these problems and data limitations, it is not surprising that large variations in emission factors across different studies are found. The outcome is that all these considerations increase the level of uncertainty in emission estimation. The situation for industrial emissions is even worse. The data on small-scale industries are grossly inadequate. The industrial emissions are potentially high but there are no reliable data to calculate the emissions. Data on other sources such as refuse-burning, fugitive dust and emissions from unpaved roads are not available.

As a part of the Urban Air Quality Management Strategy in Asia (URBAIR) project, a comprehensive emissions inventory was developed for Mumbai. It was estimated that in Mumbai, the SPM emissions amounted to some 32,400 tonnes/year for 1992/93. Road traffic, particularly re-suspension of road dust, wood burning, domestic refuse burning and the industrial use of furnace oil were the principal sources of SPM emissions (Shah and Nagpal 1997). The details on source contributions to SPM and PM₁₀ are given in the Table 6.3. The table shows that a potentially high (and hitherto undocumented) source of PM₁₀ is the burning of household waste, leaves and garbage in streets as well as in municipal waste dumps.

Table 6.3 Source contribution (%) to emissions of SPM and PM₁₀ in Mumbai for 1992

Source	SPM (%)	RSPM (%)
Thermal power plant	6	10
Gasoline cars / 2- and 3-wheelers	5	8
Diesel cars / trucks / buses	9	16
Re-suspension	40	16
Industrial fuel	7	10
Biomass burning	17	14
Marine	2	3
Refuse burning	14	23

Source: Shah and Nagpal 1997

The CPCB estimates that nearly 2000 tonnes of pollutants (which includes CO, SO₂, NO_x, hydrocarbons and SPM) were emitted daily in Delhi in 1993 (CPCB 1995).

Emissions loadings from various sectors have been increasing over time. Table 6.4 summarises the estimated pollutant emissions from various sectors. Vehicular traffic was the main source of CO and hydrocarbons, and a significant source of NO_x emissions. The estimated hydrocarbon emissions may contain large uncertainties, as other sources of hydrocarbon emissions are expected to contribute much more than 3% to the total. Thermal power stations and industries contributed significantly to TSP, SO₂, and NO_x emissions.

Table 6.4 Sectoral emissions in Delhi (tonnes/day)

Pollutant	Transport	Power	Industries	Domestic	All
TSP	13 (10%)	50 (37%)	60 (44%)	12 (9%)	138 (100%)
SO ₂	11 (6%)	121 (68%)	35 (20%)	12 (6%)	179 (100%)
NO _x	157 (49%)	143 (44%)	20 (6%)	3 (1%)	323 (100%)
CO	810 (76%)	8 (1%)	128 (12%)	117 (11%)	1063 (100%)
HC	310 (97%)	2 (<1%)	6 (2%)	2 (<1%)	320 (100%)

Note The percentage contributions are given in parentheses

Source: CPCB 1995

The CPCB points out that transport sector contributed 63% to the total emission load in 1993, expected to increase to 72% by the year 2000-2001 (MoEF 1998). These figures, however, have no technical meaning and have no policy implications. In particular, it would be incorrect to conclude from such calculations that transport is responsible for 72% of air pollution. Different pollutants have different levels of toxicity on a mass basis. In terms of health impact per unit mass concentration, CO—which is emitted in greatest quantity in sheer tonnage—is least harmful. Other pollutants, such as lead, are emitted in much smaller quantities but are considerably more harmful than CO. Taking the figures in Table 6.4, the total amount of CO is 1063 tonnes per day, whereas that of PM₁₀ is likely to be of the order of 70 tonnes per day (assuming half of TSP is PM₁₀). In terms of health impact, PM₁₀ is much more damaging than CO. But adding the tonnes of CO and PM₁₀ across sectors and merely comparing tonnage figures would lead to the conclusion that CO dominates air pollution, and because transport accounts for 76% of CO, transport correspondingly accounts for the bulk of air pollution. Examination of the TSP figures in Table 6.4 indicates, however, that for this pollutant, which is a surrogate for the pollutant of concern in Delhi—namely PM₁₀ or smaller particles—transport would still account for only 10% of the total. Assuming that nearly 100% of TSP from transport is PM₁₀, transport would still account for only one-fifth or so of total PM₁₀. While the error margins in this table may be large, one conclusion that cannot be drawn from this emissions inventory is that transport is responsible for the majority of air pollution that is damaging public health in Delhi.

The level of uncertainty surrounding particulate emission estimation in Delhi is further highlighted in a comparison of PM₁₀ emission inventories carried out by Kandlikar and Ramachandran (2000). The results are shown in Table 6.5. The large differences in emission estimates in Delhi between the two studies would suggest that uncertainties are likely to be even much higher in other cities where data are more limited.

Table 6.5 Comparison of net PM₁₀ emissions (thousand tonnes/year) from two different studies

Sector	CPCB ^a	Kandlikar and Ramachandran
Transport	5	16 – 32 ^b
Power	18.3	45 – 125
Other Industries	21.9	45 – 125
Domestic		3 – 5

Source: Kandlikar and Ramachandran 2000

^a Calculated by Kandlikar and Ramachandran (2000) from the CPCB estimates of SPM for Delhi in 1993

^b Calculated on the basis of the number of vehicles in Delhi in 1995

Gargava and Aggarwal (1999) prepared an emissions inventory for Cochin, which is a highly industrialised area situated in the southern part of India. In a systematic way the sources were broadly classified as point, line and area sources. The data on emissions from industries and fuel consumption for vehicular and domestic activities, along with the respective emission factors, were used for estimating the emissions. The study showed that industrial sources were mainly responsible for emissions of particulate matter, oxides of sulphur and ammonia in the region. Automobiles were the prime sources of hydrocarbons, oxides of nitrogen and carbon monoxide emitting 95%, 77%, and 70%, respectively of the total emissions, while the contribution from domestic sources was not very significant.

Observations from studies in other countries

There are some useful observations from other countries. As mentioned earlier, the Airborne Particles Expert Group (1999) in the United Kingdom reported that road traffic nationally contributed 25% of primary PM₁₀ emissions, but the relative importance of road traffic emissions increased with decreasing particle size and road transport accounted for an estimated 60% of PM_{0.1}. These inventories did not include re-suspended particles which cannot be reliably quantified at this time. The same report mentions that the particle number, which reflects mainly PM_{0.1}, is a very good tracer of road traffic emissions in urban areas, and more closely related to road traffic than PM₁₀ mass. In a handful of cities studied in the United Kingdom, diesel vehicles contributed much more to the particle number than gasoline vehicles, and significantly more than was indicated by the urban road transport mass-based PM₁₀

inventories. Because small particles are believed to be much more damaging to health than coarse particles, these findings point to the importance of not drawing policy conclusions solely on the basis of PM_{10} , let alone TSP, inventories.

The population density and particulate emission characteristics of gross polluters in the transport sector were investigated in a recent study conducted in the South Coast Air Quality Management District in California (Durbin *et al.* 1999). Gasoline-fuelled passenger cars were found to emit as much as 1.5 g/km, emission levels normally associated with diesel vehicles. Between 1% and 2% of the light-duty vehicle fleet in the South Coast Air Quality Management District was estimated to be gross polluters, but they contributed as much as one-third to the total light-duty particulate emissions. It is possible that the proportion of “smoking” gasoline vehicles is much larger in South Asia, and hence the need to have better data for emission factors and the number of contributors.

Finally, an example of careful data collection and analysis confounding the conventional wisdom is given by a study in Colorado which undertook, amongst others, an examination of source contributions to $PM_{2.5}$ (Watson *et al.* 1998). The available emissions inventory indicated that diesel accounted for two-thirds of on-road vehicle $PM_{2.5}$ emissions and gasoline the remaining one-third. However, extensive data collection and the use of the chemical mass balance model found that diesel actually accounted for only a third and gasoline two-thirds, and that $PM_{2.5}$ emissions from gasoline vehicles were seriously under-estimated, both with respect to diesel and on an absolute basis. The discrepancy was mainly due to the presence of gasoline “smokers” and high emissions during cold start. It is worth keeping in mind these points challenging the conventional wisdom in formulating policy for urban air quality improvement.

Air quality modelling

Dispersion modelling

IIT line source (IITLS) model, a line source model developed at the Indian Institute of Technology (IIT), Delhi, was used to describe the downwind dispersion of pollutants near roadways along with CALINE-3, the California line source dispersion model (Goyal and Krishna 1999). Both models were based on the Gaussian plume methodology and were used to predict the concentrations of air pollutants near roadways. The parameters for the IITLS model, such as the source strength and dispersion parameters, were estimated from routine data available in urban Delhi. In order to test the performance of the IITLS and CALINE-3 models, the NO_2 concentrations at three heavy traffic corridors in Delhi—the ITO, Parliament Street

and Pahar Ganj—were compared against measured air quality data. Statistical error analysis of both model calculations and measured concentrations was carried out. The analysis showed that the performance of the IITLS and CALINE-3 models was comparable and the model outputs were in agreement with the measured concentrations.

Sivacoumar and Thanasekaran (1999) undertook a study to identify the mathematical model that could be most useful for calculating pollutant concentrations near roadways. A Gaussian-based finite line source model was employed to predict pollutant concentrations due to automobiles on roadways. The model was applied to four sections of a major highway in Madras, the capital city of Tamilnadu, to model CO concentrations. Comparison of model outputs and measurements was performed using both quantitative data analysis techniques and statistical methods to evaluate model performance. The analyses indicated that the model performance was good.

There are many ways of estimating the source strength, the most crucial parameter of a given model. In a study conducted in Delhi (Goyal and Krishna 1998), four different methods of source estimation of vehicular traffic were used. These methods were evaluated by the IITLS model. The ground level concentrations of NO₂ were modelled using the IITLS model in which emission rates were calculated using these methods. The outputs from the IITLS model were compared with measured NO₂ concentrations at two places in Delhi. The model outputs using different methods were checked by five statistical performance measures. The study findings showed that the model outputs using the first three methods of emission estimation were in agreement with the observed NO₂ concentrations and were also well correlated with each other. Thus first three methods were considered to be appropriate for estimating NO₂ emissions from vehicular traffic. On the basis of available traffic data, method 3 was found most suitable for Indian urban cities.

The outputs from two line source models based on Gaussian formulation were compared to measured airborne lead concentrations at 13 busy intersections in Delhi (Goyal *et al.* 1995). This study modelled lead concentrations due to vehicular traffic over the next 10 years, assuming no change in the content of lead in gasoline⁵.

CO concentrations due to vehicular traffic in urban Delhi were computed by using an analytical dispersion model (IITCO), Pollution Episodic Model (PEM) and Intersection Midblock Model (IMM) (M.P. Singh *et al.* 1988b). While IITCO was developed at IIT, the other two are operational models from the United States. Computations from the models were compared with measured concentrations at ITO,

⁵ Lead in gasoline was phased out in Delhi in 1998.

Janpath, Nazafgarh and Townhall. On-site measurements of CO were taken by using real time analysers and meteorological parameters were obtained from a micrometeorological tower at IIT, Delhi. The model results compared well with the measurements. The performance of IITCO was compared with PEM and IMM and found to be quite satisfactory.

In a similar study, three air pollutants—SO₂, SPM, and NO_x—were considered for a study comparing calculated and measured concentrations at different receptor points in Delhi (M.P. Singh *et al.* 1988a). A receptor-oriented Gaussian plume model (IITLT) and Climatological Dispersion Model (CDM) were used to estimate the long-term concentrations of non-reactive pollutants (SO₂ and NO_x were assumed to be non-reactive) due to emissions from area and point sources. Modified stability parameters were used for low wind speed and calm intervals. The monthly mean concentrations of these pollutants for the period of November 1987, December 1987 and January 1988 were computed and the results obtained from the two models were found to be close to the measured concentrations for this period. Error analysis of 54 pairs of measured and model-calculated concentrations showed that the performances of both models was highly satisfactory, giving a root mean squared error of 1.61 for IITLT Model and 1.50 for CDM.

A group in Calcutta attempted to validate Johnson's Street Canyon model for NO₂ (Chakrabarty, Sarkar and Biswas 2000). The model was validated for one dual carriage-way. Background (8th floor of a building) and kerbside concentrations for NO₂ were measured simultaneously for most of the sampling days for two hours each day. The authors concluded that the model was reliable, because the coefficient of correlation between calculated and measured values was 0.48.

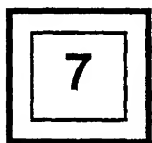
In Mumbai, Gokhale and Patil (2000) developed a general finite line source model for the prediction of size-separated aerosols and lead concentrations from vehicular sources. The calculated values were compared with the measured values at two traffic sites. One site was near a busy traffic intersection and other one was near a road with a moderate traffic flow. The model under-predicted particles in the size range 10 µm – 3.3 µm and over-predicted those smaller than 3.3 µm. The authors speculated that the difference might be because of the contribution of the re-suspended dust in the measured concentrations in the former case and the escape of smaller particles from the samples collected for measurement in the latter case.

Time series modelling

Historical time series data of CO concentrations in Delhi were analysed using Box-Jenkins modelling approach (Sharma and Khare 2000). Univariate linear stochastic models (ULSMs) were developed to examine to what extent modelling could match

measured concentrations in situations where only limited data are available. The models developed were used to provide short-term, real-time forecasts of extreme CO concentrations for an Air Quality Control Region (AQCR), comprising a major traffic intersection in a central business district in Delhi. In another paper by the same authors (Sharma and Khare 1999), an intervention analysis model (IAM) was developed to study the impact of the “intervention” introduced by the Government of India (GoI) to control the CO pollution caused by vehicular exhaust emissions—the enforcement of the emission standards for the vehicles—on the mean level of the time-series CO concentration data. The study was conducted for an Air Quality Control Region (AQCR) comprising an urban road intersection in Delhi, where vehicular traffic accounts for almost all of CO emissions. Application of the model suggested that the ‘intervention’ had not been effective in bringing down the level of ambient CO; the authors offered some likely explanations.

A time-series analysis of SPM concentrations in Mumbai was performed using the recursive algorithm (Chelani *et al.* 2000). The Kalman filter was used to estimate the system parameters. The algorithm was found to be able to analyse the time-series data accurately. The algorithm was further developed to predict concentrations at three sites, and gave a good fit. The trend was found to be that of increasing SPM concentration. The seasonal and cyclical variability in time-series SPM concentrations at three sites illustrated that local sources were significant at the sites. The authors speculated that more accuracy could be obtained by the inclusion of variables such as meteorological and emissions factors in the model.



Recommendations

- Data :
 - A sufficiently large number of samples should be collected so as to permit statistically valid evaluations. The nature of the distribution—whether binomial, geometric and so on—should be determined from a large data set. Statistical parameters such as standard deviations and other measures of variance must be reported to enable an accurate interpretation of the data.
 - Differences in levels of pollutants measured at different sites in urban locations are often cited in studies. Rarely, if ever, are statistical tests carried out to confirm that the variance is inherent in the data.
 - Environmental data are known to follow log normal rather than binomial distributions. Parallel tests for analysis of variance are available and must be used wherever appropriate.
 - PM_{10} and $PM_{2.5}$ rather than TSP should be monitored regularly in light of emerging epidemiological evidence concerning the health impact of different size particles.
- Background air quality data
 - Only a very few studies characterise regional and background areas. It is incremental concentrations relative to the background that air quality management policy measures can target. Collecting background air quality data is essential for understanding measurements in cities and characterising the nature of ecosystems unique to India.
- Tracers
 - One of the important aspect of air pollution studies is the establishment of specific tracers for sources. Statistical methods of analysis may confuse or even mislead at times if the right tracers are not properly included. Many studies have been limited by the instruments available, so that the right tracers could not be analysed. A systematic approach to identify key tracers in India and then to carry out studies including all the major tracers would be helpful. In this regard, there should be special efforts made to analyse carbon (black and organic) in PM_{10} or finer particles, to be followed eventually by hydrocarbon speciation for source identifications.
- Analytical protocol:

- The methods of sampling, sample handling and analysis should be described in great detail including the manufacturers' names and model numbers. Especially if the methods used in a study differ from standard or commonly used procedures, they should be outlined so that the results can be interpreted accordingly. Blanks (such as field blanks and filter blanks) must be analysed at each stage of sampling. Accuracy, precision, and the detection limits of the method and instruments used must be explicitly reported.
- The number of samples taken, the hours of exposure, meteorological conditions (temperature, relative humidity, wind direction, wind speed, solar insolation, cloud cover, rainfall) during the sampling period, and parameters such as the flow rate, filter materials and filter holders should be reported.
- The time gap between sampling and analysis should be as small as possible barring conditioning of filters for particulate matter. Where samples have to be transported from remote regions to central laboratories, appropriate measures such as freezing can be taken.
- The correct handling and storage of samples is vital. Several reports published in international journals recommend the addition of preservatives such as thymol or chloroform to samples to prevent microbial degradation. If elements are to be analysed in samples of fresh water or rainwater, it is recommended that high density polyethylene containers washed with detergent followed by a 24 h soak in 10% nitric acid be used. This will prevent the adsorption of the cation species on to the walls of the container. Such pre-treatment of containers used for storage is rarely mentioned in Indian studies.
- Recording of other data
 - Meteorological variables, radio sonde data and so on are extremely important in mapping the trajectories of plumes from industrial areas and flows in urban areas, specially for species such as ozone. Variables such as the mixing height, boundary layer height and inversion height are important determinants of critical levels of air pollutants.
- Collaboration among researchers
 - Most studies from India tend to be the individual effort of researchers at different institutions. Inter-laboratory collaboration is an excellent way to evaluate the accuracy and validity of the data collected. Field samples as well as blind test samples and standards can be exchanged after establishing set protocols among laboratories.
 - In a manner distinctly different from what is prevalent, laboratories should also exchange data without inhibition. This will prevent duplication of efforts and may also augment the value of the data.

- Software for data analysis
 - It should certainly not be difficult for an IT-rich country such as India to produce the software required for database management and environmental studies. Ever so often, researchers are discouraged from using methods such as PCA and factor analysis for the lack of the software. Statistical packages are also extremely useful and it should be feasible to develop these without much trouble.
- Literature surveys
 - In order to present a comprehensive review of the parameters and areas of interest in the Indian context, the bibliography quoted in a paper should be complete. Many Indian studies omit or neglect to mention other Indian studies. Bibliographies in the context of India are rarely, if ever, exhaustive. With better methods of communication today, this should be an easily circumvented obstacle.
- Inventories
 - A list of sources peculiar to the urban environment in India must be formulated and quantified. This should be carried out for both biogenic and anthropogenic sources. For example, a large variety of biomass (cow dung, crop residues and firewood) is used in India even in urban areas, greatly influencing the quality of air in cities. A knowledge of the quantity and nature of species evolved or emitted will help in drawing up budgets, and thus standards.

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